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Prof. C. V. RAMAN, M.A., Hon. D.Sc., F.R.S.

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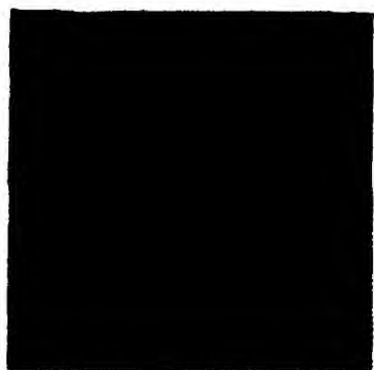
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PLATE I



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RINGS SHOWN BY REFLECTED AND SCATTERED LIGHT.

# 1

## Infra Red Emission and Absorption of Potassium Vapour

By

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AND

D. GUNNAYYA, M.A.

### CONTENTS

Introduction

Experimental Details.

(a) Emission Spectrum.

(b) Absorption Spectrum.

Discussion of results.

Summary and conclusions.

In spite of the excellent and more recent investigations the whole matter of the origin of spectral lines seems to be in a state of confusion as can be readily seen from the conflicting views advanced by Saha, Hemsalech, Seeliger, etc. For, Saha<sup>1</sup> published a series of papers on the theory of thermal ionisation and thermal radiation of gaseous elements and proposed a physical theory of stellar spectra, where the author discussed the problem of atomic dissociation from the thermodynamic standpoint. By means of Nernst's heat theorem, and the equation of the "reaction isobar" the author calculated the degree of ionisation for a number of elements at different temperatures and under different pressures from which he attempted to find to what extent atomic dissociation

<sup>1</sup> M. N. Saha "Ionisation in the solar Chromosphere" (A) Phil Mag., October, 1920, "Elements in the Sun" (B), December, 1920, "On the Temperature Radiation of Gases" (C), February, 1921.

into positively charged atom and electrons was possible in sun and different stars. Eddington<sup>1</sup> while dealing with the role of radiation pressure in the constitution of stars incidentally suggested that elements may be ionised owing to high temperature. This fact was also independently suggested by Jeans.<sup>2</sup> According to the views advanced by these authors the energy necessary for excitation of the spectral lines of an element is in the order : principal series ; diffuse series ; sharp series ; Bergmann series ; etc. Hemsalech<sup>3</sup> from a series of investigations has reached conclusions which differ materially from the views advanced by the foregoing authors.

He (Hemsalech) thinks that the emission of spark lines is connected with the existence of strong electric fields and is further of opinion that King's tube resistance furnace spectra are not of a purely thermal origin. While Messrs. Seeliger and Thaer<sup>4</sup> investigated the arc and spark spectra of the alkalis where it was shown that the energy necessary for excitation of the arc lines of an element is in the order : Bergmann series, principal series, diffuse series, sharp series, etc., and they add that it is significant that in its entire behaviour the Bergmann series, of the whole arc series, is furthest removed from the spark series. Thus the lines of Bergmann series, according to Seeliger, are associated with the *normal* atom of the element. As regards the question of the reversal of lines, at low temperatures only the lines corresponding to the combination  $1, s - m, p$ , are absorbed. While the lines belonging to the diffuse series, Bergmann series, etc.,

<sup>1</sup> Eddington, 'M. N. R. A. S.', Vol 77, pp. 16 and 500, Vol 79, p. 2; and Observatory, No 557, pp 341-358, October, 1920

<sup>2</sup> Jeans - 'M. N. R. A. S.', Vol 79, p 319

<sup>3</sup> Hemsalech - 'Comptes Rendus' 169, pp 915-918, November 17, 1919.

" 169, pp 1034-1036, December 1, 1919

" 170, pp. 31-38, January 5, 1920.

Science Abstracts, Sec A, 1981, December, 1921.

" " " 130, December, 1922.

Phil Mag, February, 1922.

<sup>4</sup> Seeliger and Thaer "An de Physic," 1921, IV, 65, pp 423-448.

would be absorbed at higher temperatures, or under electrical stimulus. But according to Seeliger's views, temperatures necessary for the reversal of the lines of different series increases in the order: Bergmann series, principal series, etc., thereby showing that the lines of the Bergmann series should be absorbed before the absorption of the principal series begins. If therefore in an absorption experiment it can be shown that the Bergmann lines would be first absorbed, we shall have to revise a good deal of our view regarding atomic structure and the origin of the spectral lines. The subject of Infra-red absorption has therefore an important bearing on the question of temperature radiation and the origin of spectral lines. It is therefore necessary by studying the absorption spectra of the alkali metals to ascertain as fully as possible the frequencies which are associated with the atom of the element in definite physical states, especially in the Infra-red region. Perhaps on account of the difficult technique, the spectroscopic study of the transparency of the vapours of the alkali metals to heat waves has been left in the back ground. The main purpose of this investigation is therefore to study the absorption of potassium vapour in the infra-red region and to find if Bergmann lines would be absorbed and if so at what temperature.

With a view to proceeding in this direction some preliminary experiments were made by the authors on the emission lines in the spectrum of potassium vapour in the same region. This was previously investigated by Becquerel, Snow, Coblentz, Paschen, Moll, Bergmann, etc. Most notable among these were the experiments of Coblentz,<sup>1</sup> who worked with a rock salt prism, and a radio-meter; W. J. H. Moll<sup>2</sup> examined the emission spectrum, using for the purpose a rock salt prism, a thermopile and an automatic device for recording the galvanometer deflections. With the automatic device

<sup>1</sup> Coblentz "Supplementary Investigations of Infra-Red Spectra," 1908.

<sup>2</sup> W. J. H. Moll, "Proceedings Amsterdam Acad.," pp 541-548, 1907



he was able to explore the region beyond  $2\mu$  more thoroughly than was possible by making personal observations. Some time later Paschen<sup>1</sup> investigated the same problem with a concave grating and a linear thermopile, while Bergmann<sup>2</sup> investigated by the photographic method. Although with the rock-salt prism spectrometer such a high dispersion as in Paschen's investigation cannot be obtained, with the linear thermopiles of the most sensitive type recently made, by Adam Hilger Ltd., and the highly delicate Paschen galvanometer made by the C.S.I. Co., seemed to justify another attempt to study the emission of potassium vapour in the Infra-red.

For studying the emission spectrum in some experiments pure potassium chloride previously well-dried, and powdered, was used in the carbon arc, using for the purpose hollowed out carbon electrodes filled with the salt, and a direct current of 12 to 15 amps. was used for the purpose. Subsequently it was found convenient to use small lumps of the metal itself in a type of the carbon arc modified by the writer of the paper. (Plate No. I.) A slightly different form of this



<sup>1</sup> Paschen Ann. de Physik. 27, pp 537-570, 1908  
Do. Do, pp 717-739, 1910

<sup>2</sup> Bergmann Wiss Photogr. 25, pp 113-145, 1908

arc was used by Hemsalech and the Compté du Gramont in their investigations on the arc and spark lines. This type was found to be specially serviceable in studying the spectra of metals having low boiling points. As is seen from the photographic reproduction the upper carbon is surrounded with a water box through which there was a constant circulation of cold water, thereby preventing the temperature of the electrode from becoming very high, and the lower electrode consists of a copper plate 8 cm. in diameter with a small depression in the middle to contain the metal or the salt in question. The whole arrangement was found to be so satisfactory that much larger galvanometer deflections could be obtained than by the first method.

The rock-salt spectrometer and the linear thermopile used in these experiments were made by Adam Hilger Co., a diagram of which is given at the end. It was of the constant deviation type, with Wadsworth mirror prism combination. The instrument was furnished with two symmetrical slits, each having an effective length of jaw of 20 mm. Light entering from the first slit  $S'$  is collimated by a nickel-steel concave mirror  $M'$ , and then passes to the rock-salt prism (32 mm.  $\times$  42 mm.) to a nickel-steel plane mirror  $M''$ , from which it is reflected to the second concave mirror by which an image of the spectrum is depicted on the second slit just behind which there is the linear thermopile. The entire thermopile was protected from extraneous radiation by a nickel-plated case. The helical drum by the rotation of which different parts of the spectrum can be brought into coincidence with the linear thermopile was calibrated in wave-lengths from  $5\mu$  to  $9\mu$ . Energy measurements were made by the linear thermopile in conjunction with a Paschen Galvanometer, made by the C.S.I. Co.

*Paschen Galvanometer.*—The magnet system consists of two groups of 13 magnets each, the magnets being arranged alternately on opposite sides of a fine glass stem which

supports also a very thin glass mirror. The whole moving system of this galvanometer weighs about 28 to 30 m. gm. A special feature of the instrument is the winding of the coils which are graded so as to have the best cross-section. The coils are elliptical in shape and are wound in such a way as to obtain the maximum field for the given resistance. The galvanometer is extremely sensitive to temperature changes. In order to obviate this difficulty, the instrument was covered with a thick layer of absorbent cotton all round.

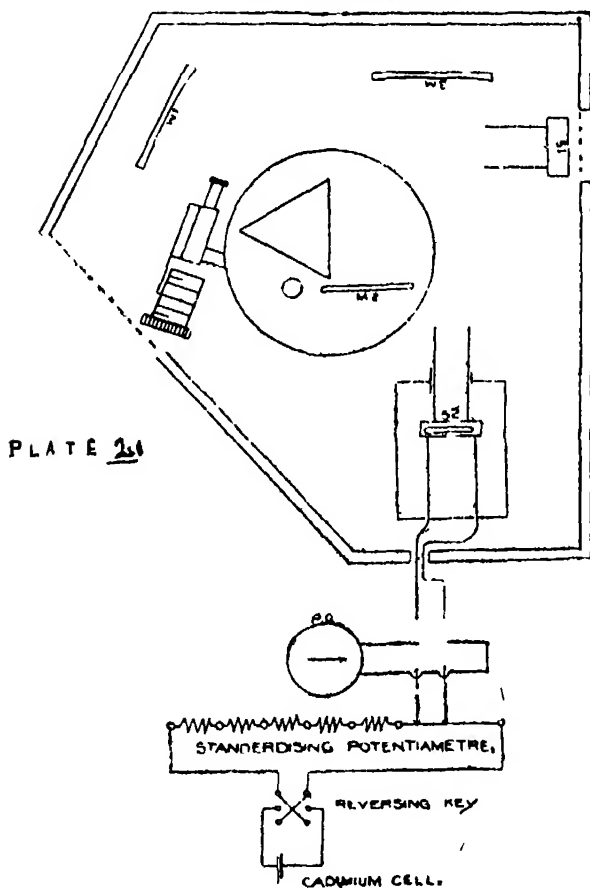
*Thermopile.*—In this linear thermopile the Hutchins alloys (Bismuth-tin, and Bismuth-antimony) were used, and it is found that this has a sensitiveness nearly 50% greater than the previous model, and is almost entirely free from creep. The dimensions of the sensitive area are 20 mm.  $\times$  1.5 mm. The number of junctions is 20, and the resistance is 12 ohms. approximately.

The period of the galvanometer in field was 6.5 seconds nearly, the coils being connected in series. The deflection at 1 metre distance for one micro-ampere was about 360 cm. with the 1 coils in series, the resistance was 12 ohms.

Before the nickel-plated case was screwed in position, the thermopile was removed and the eye-piece, which is attached behind the slit S'', was mounted in position and sun-light was directed on to the slit of the spectrometer by means of a heliostat, and the solar spectrum was obtained. The eye-piece was focussed on the Fraunhofer lines, and the slit width was adjusted so that the radiation at S'' was in agreement with the reading on the wave-length drum. In this way, settings were made for B, D, E, and F lines of the solar spectrum. The instrument was similarly standardised in the long wave region by means of the absorption bands of water, using for the purpose a layer of water of .5 to 1 mm. in thickness so that the bands are sharp and well-defined. Having thus standardised the instrument, the eye-piece was

removed, the thermopile placed in position, and the nickel-plated case was screwed in its place.

—PLAN OF THE INFRARED SPECTROMETRE—  
—PASCHEN GALVANOMETRE AND TESTING—  
—POTENTIOMETRE—



To avoid stray air currents and consequent changes in temperature, the whole spectrometer was enclosed, as will be seen from the diagrammatic plan (Plate II), in a box furnished with two windows, one in front of the collimator

slit and the other near the wave-length drum. The box was painted inside with black varnish, and outside with white enamel. The outside of the box was further covered with a layer of asbestos cloth, and the space inside with layers of cotton wool. To keep the air surrounding the rock-salt prism free from aqueous vapour, dishes containing fused calcium chloride and phosphoric anhydride were placed round the spectrometer.

In the first stages of the work, in spite of these precautions very great difficulty was experienced in making energy measurements owing to want of steadiness in the zero of the galvanometer. Sometimes though there was absolutely no radiation falling on the slit of the spectrometer the spot of light used to oscillate over a range of 4 to 5 cm. even these oscillations being quite irregular and sudden. It was subsequently found that the hot summer winds were the cause of these sudden fluctuations in the zero of the instrument, and to overcome these difficulties it was found necessary to work in the early hours of the morning from 4 to 8, when there was a perfectly calm and cool atmosphere. Under these conditions it was found that the zero of the galvanometer was perfectly constant even though the full scale deflections were obtained on certain occasions. In investigating the emission spectrum, quite a large number of readings was taken to establish the exact position of the maxima. The wave-lengths of the lines found in this investigation are given in the following table (No. I), along with the lines found by other investigators.

From a comparison of these values it will be seen that the values given by Moll, are consistently slightly higher than those of the author, which is probably due to the method adopted by Moll for automatically recording the galvanometer deflections. The line  $1.19\mu$  corresponding to which there is none in the observations of the other investigators is probably a new one.

TABLE NO. I.

Authors	Paschen	Moll	Beigmann
		10,400	
		27,360	
36,700		31,460	31,800
30,500		27,600	
	27,215		
27,150	27,065		
		15,300	
15,280			15,282
	15,165		
12,500	12,523	12,500	12,507
	12,134		12,415
11,900			
11,750	11,771	11,800	11,762
11,600	11,689		11,678
11,000	11,028	11,100	11,012
10,800			
9,620		9,700	9,500
			8,908
			8,500

The line  $3.67\mu$  is obviously the combination line  $2, p-3, s$  being the same as the line  $3.7\mu$  found by Moll, but not recognised by the later investigators. The line  $2.72\mu$  is the combination line  $2, s-3, p$ , and corresponds to  $2.72$  and  $2.71\mu$  found by Paschen by the concave grating. The lines  $1.175\mu$  and  $1.25\mu$  are the first members of the diffuse and the sharp series respectively.

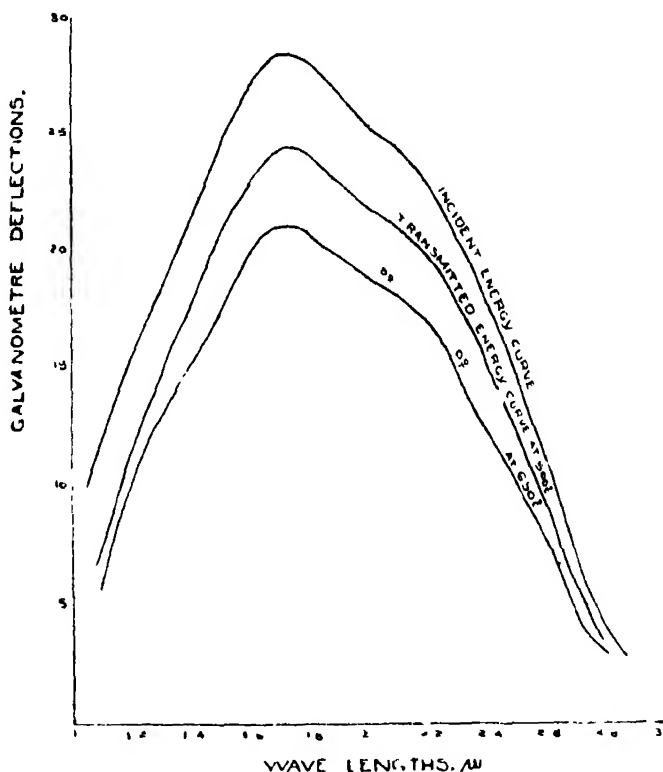
*Absorption in the Infra-red.*—For studying the absorption in this region, the method adopted was essentially the same as that used by the authors in their experiments on "The absorption of Potassium vapour in the visible and the ultra-violet." Only, instead of an arc lamp a metal filament lamp was used as the source of light. And to protect the thermopile from extraneous radiation there were placed between the slit of the spectrometer and the source of light 4 co-axial card-board diaphragms pierced with apertures about 1" in diameter. A pretty large quantity of the metal was enclosed in the steel tube which was then filled with pure dry hydrogen. After subjecting the tube to a preliminary heating

up to about  $350^{\circ}\text{C}$ . the tube was connected to an air pump and was exhausted to  $\cdot 5$  cm. When the tube cooled down to the room temperature observations were made first on the emission spectrum of the metal filament lamp. Then the tube was heated and the enclosed metal was vaporised in the manner

TABLE NO. II.

u	GALVANOMETER DEFLECTIONS IN CMS			Transmission percentage for 500.
	Incident energy.	Transmitted energy at 500	Transmitted energy, at 650	
1 0	8 00	2 00	0 35	25 0
1 1	12 10	7 40	6 65	61 0
1 2	16 00	11 50	10 10	72 0
1 3	18 00	14 05	12 85	83 0
1 4	20 75	17 20	15 00	83 0
1 5	24 20	20 50	17 20	85 0
1 6	27 00	22 70	20 06	84 0
1 7	28 45	24 20	20 10	85 0
1 8	28 30	24 30	20 70	86 0
1 9	26 80	23 00	19 60	86 0
2 0	25 45	22 0	18 90	86 5
2 1	24 60	21 20	18 10	86 5
2 2	23 00	19 90	17 25	86 5
2 3	20 50	17 50	14 85	86 0
2 4	18 00	15 50	13 50	86 0
2 5	14 90	12 70	10 10	85 0
2 6	11 15	9 50	7 95	85 5
2 7	7 00	6 10	4 55	86 5
2 8	3 80	3 30	3 21	86 7
2 9	2 50	1 90	1 70	76 0
3 0	1 20	0 95	1 00	80 0

explained in the previous experiment, and observations were made of the transmission spectrum at different temperatures, the maximum temperature used by the authors being about

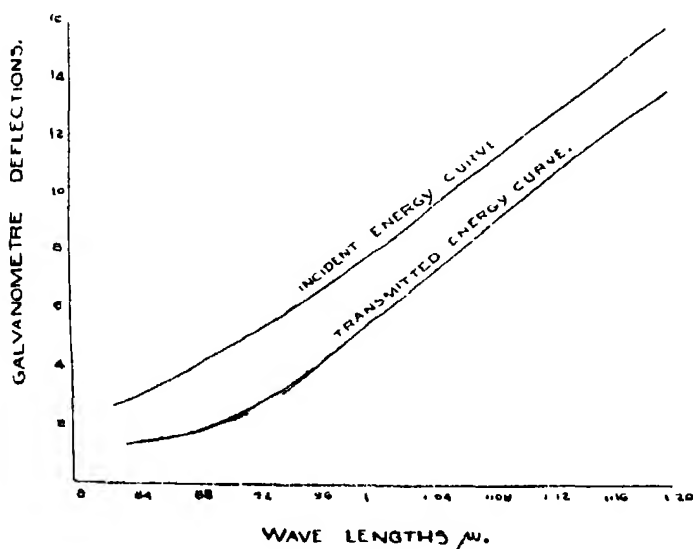


700°C. At higher temperatures it was found practically impossible to maintain the vapour at a constant density chiefly due to the distillation to colder parts. The Galvanometer deflections which were proportional to the incident and transmitted energy are given in Table II, above, for two different temperatures 500 and 650 degrees centigrade roughly. At both these temperatures, as the galvanometer deflections for wave-lengths below  $1\mu$  were too small to be relied upon, they were not recorded. But as these experiments were mainly intended to find if Bergmann lines ( $1.517\mu$ ;  $1.103\mu$ ;



$\cdot 96\mu$ ; and  $\cdot 89\mu$ ) would be absorbed by the normal atom, in order to study the region  $\cdot 8\mu$  to  $1\cdot 2\mu$  more thoroughly energy measurements were made at a lower vapour density by reducing the temperature of the tube the results of which are given in Table III below.

Incident and transmitted energy curves were drawn by plotting the galvanometer deflections against the wave-length values from which it is clear that the vapour does not exercise any selective absorption in the infra-red region, at any rate below  $600$  or  $650^{\circ}\text{C}$ ., but that the absorption at  $\cdot 77\mu$  (the first member of the principal series) extends gradually to the long-wave-length side also with increase of temperature as is clearly seen from the transmission percentage values calculated for temperature  $500^{\circ}$  in Table II, and also for wave-lengths between  $\cdot 77\mu$  and  $1\cdot 2\mu$  in Table No. III.<sup>1</sup> It is therefore beyond doubt that the lines of the principal series are the first to be absorbed as the temperature is gradually raised. In this



<sup>1</sup> Pls. 3 and 4

TABLE NO. III.

$\mu$	GALVANOMETER DEFLECTIONS IN CMS		Transmission percentage
	Energy incident	Energy transmitted	
0.77	1.70	0.60	35.00
0.80	2.30	1.00	43.00
0.82	2.60	1.20	44.00
0.84	3.00	1.35	45.00
0.86	3.50	1.50	43.00
0.88	4.00	1.75	43.00
0.90	4.60	2.00	43.50
0.92	5.25	2.40	45.70
0.94	5.95	3.20	53.70
0.96	6.50	4.00	61.00
0.98	7.35	4.70	63.80
1.00	8.00	5.70	71.00
1.02	8.70	6.30	72.30
1.04	9.50	7.10	74.60
1.06	10.10	6.20	78.70
1.08	11.20	9.15	81.50
1.10	12.10	10.10	83.40
1.12	12.90	10.70	83.00
1.14	13.60	11.55	85.00
1.16	14.40	12.30	85.40
1.18	15.10	12.90	85.60
1.20	16.00	13.70	86.00

connection it is also interesting to note that as a result of experiments conducted by the authors (described in the previous pages) at high temperatures with a view to study the absorption of the vapour, it was found that there were distinct traces of absorption in the diffuse series at about 1100°C.

The thermopile however thin it may be usually occupies a few Angstrom Units in the spectrum when it is made to pass through the whole range. When the absorption line is broad as in the case of the principal series the junction may be completely covered by the line, and comparatively lesser deflection is obtained. But if we are dealing with a faint and narrow region of absorption the junction covers not only this faint and narrow region of absorption but also the surrounding region of free transmission. Hence the effect of absorption may be completely lost when examined by the

thermopile. It was therefore thought that the photographic method would be more decisive.

For photographing the spectrum in this region the plates were sensitised for the red and the infra-red region with pinacyanol according to a recipe given by Prof W. J. Pope of the University of Cambridge :—

50 c.c. of distilled water.

25 c.c. of alcohol

1 c.c. of 1% alcoholic solution of Pinacyanol.

A "Special Rapid" Illford plate was bathed in such a solution, in absolute darkness for about 3 minutes, and then quickly dried before a table fan. With long exposures, the plates were found to be sensitive up to  $0.9\mu$  though the sensitiveness diminishes rapidly from  $0.8\mu$ . By using a reflection grating with 30,000 lines the spectrum was photographed in the first order which shows no traces of absorption at  $0.89\mu$  and  $0.85\mu$  of the Bergmann series.

These experiments go to show conclusively that the temperature necessary for the reversal of lines of different series increases in the order: principal, diffuse, etc.

#### *Summary and Conclusions.*

(1) The existence of the line  $3.65\mu$  and  $2.72\mu$  which were found by Moll and Paschen respectively but not found by later investigators has been confirmed and a faint new line was found at  $1.2\mu$ .

(2) The absorption spectrum of the vapour in the infra-red has been studied and it has been found that the non-luminous vapour does not exercise any selective absorption.

(3) The importance of the study of absorption in the infra-red by the non-luminous and luminous vapours on the problem of temperature radiation and the origin of the spectral lines has been shown.

H. H. THE MAHARAJA'S COLLEGE, VIZIANAGRAM.

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## 2

# Absorption of Electrically Luminescent Potassium Vapour.

BY

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AND

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## CONTENTS.

Introduction

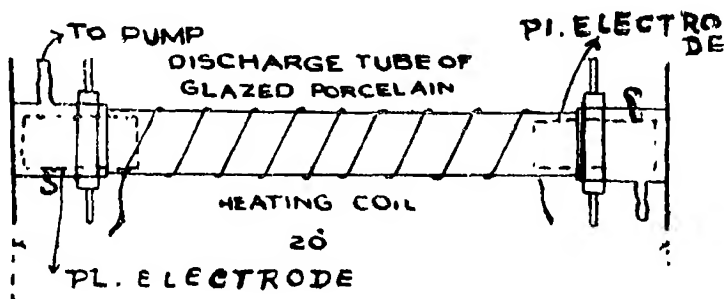
Experimental Details

Discussion of results

## INTRODUCTION.

It has been pointed out in the paper on "Infra-Red Emission and Absorption of Potassium" that for the vapour of an element to absorb light corresponding to a given series in its spectrum, it is necessary that in the vapour there should be a fairly large number of atoms with orbits corresponding to the first term of the pulse of radiation to be absorbed, *i.e.*, the atom should be in that one of the two states possessing the smaller energy value. For the lines  $2, p-3, d: 2, p-m, s$ ; or  $3, d-4, f$ , to be absorbed it is necessary that there should be a sufficient number of atoms with  $(2, p)$  or  $(3, d)$  orbits. According to our ideas of the origin of spectral lines, energy necessary for the excitation of the lines of the Bergmann

series is greater than that of the diffuse and the sharp series. The lines of the Bergmann series therefore begin to be absorbed at high temperatures, *viz.*, at the temperature of emission of the sharp series. As it is very difficult to obtain the very high temperature necessary for the reversal of the lines of this series in the laboratory except by King's tube resistance furnace, it was thought convenient to adopt the alternative method of keeping the vapour in a feebly luminescent state.



*Experimental arrangement.*

The discharge tube consists of a glazed porcelain tubing about 50 cm. long which was fitted with two brass fittings cemented to the tube<sup>1</sup> at the two ends with best sealing wax. Each of these contained as will be seen from the figure 5 a water box for constant circulation of water, and a side tubulure. These were provided at the ends with plane plate glass windows and the discharge passed between two cylindrical electrodes of platinum. The tube was wrapped with a heating coil thoroughly covered with some layers of asbestos paper by which the temperature could be maintained uniform. By means of an automatic Sprengel pump made for the purpose, the tube was exhausted to a pressure of the order

<sup>1</sup> This tube was kindly lent to the writer by Mr. V. Apparao, Prof. of Physics, Government Arts College, Rajamandry, to whom his best thanks are due.

of  $\cdot 001$  mm., and the interposition of a long phosphorous pentoxide tube between the pump and the discharge tube was found to suppress the mercury lines effectively. And under this high vacuum, pure potassium vapour was distilled into the discharge tube from the other side tubulure. For studying the absorption the mirror spectrometer and the Paschen-Galvanometer described in detail in the previous pages were used as all the lines of the Bergmann series are in the long wave region. When the discharge tube was mounted before the slit of the spectrometer and the discharge from a small induction coil was passed through the vapour, it was found that the Galvanometer was seriously affected by the presence of the powerful electro-magnet of the induction coil. Finally the absorption tube was therefore mounted at a distance of 30' from the spectrometer and the galvanometer, and a beam of sun-light directed into the dark room by means of a heliostat set in motion by clock work, was brought into a focus at the centre of this tube by a long focal length lens. After emergence from the tube, the beam was made to pass through a number of diaphragms on its way to the slit of the spectrometer. With the induction coil at this distance, the Galvanometer was not affected even to the slightest extent when the coil was excited. The vapour being maintained at a temperature of about  $350^{\circ}\text{C}$ . before the discharge was passed through the vapour, galvanometer deflections were noted between 1 and  $1\cdot 5\mu$  at intervals of  $\cdot 01\mu$  as this region contains the first members of the diffuse and sharp series of potassium, *viz.*,  $1\cdot 18\mu$  and  $1\cdot 25\mu$  and the first two members of the Bergmann series  $1\cdot 52\mu$  and  $1\cdot 1\mu$ . The vapour was then raised to feeble luminescence by passing the discharge from a small coil and galvanometer deflections were noted in the same region. On account of the low value of the ionisation potential of this element, even this feeble excitation was sufficient to make the vapour emit the lines  $\cdot 58\mu$  and  $\cdot 53\mu$  belonging to the diffuse and the sharp series.

above a certain temperature called the critical solution temperature are perfectly miscible and form a single phase but below which are only partially soluble and divide into two co-existent phases. They also found that such mixtures exhibit a marked opalescence or turbidity at a temperature slightly higher than that at which they separate into two layers. As their primary object was the study of mutual solubility of mixtures, their observation was restricted to the observation of the phenomenon of critical opalescence. Further work on the subject was done by Konowalow<sup>1</sup> who investigated the connection between the opalescence and variations in the partial vapour pressures, these variations being the most important criterion of solution. The results which he obtained for solutions of aniline and amylene in the critical range showed a similarity between these and colloidal solutions, the dependence of the vapour pressure on the concentration of the solutions being very small. He finally adopted the view that the opalescence of liquids is due to dust and that the increased opalescence in the critical range is due to the greater facility with which the components separate in this region and condense on the dust nuclei. As we shall see later, this conclusion of Konowalow is not true, as the opalescence is obtained even in the case of dust-free liquids. So far the observations were more or less of a qualitative nature, no attempt having been made to observe the amount of light scattered by the liquid mixtures.

It was after Smoluchowski<sup>2</sup> and Einstein<sup>3</sup> gave a theory to explain the critical opalescence of liquid mixtures, that quantitative measurements were made by Fürth<sup>4</sup> for the mixtures of phenol and water and Zernike<sup>5</sup> for the mixtures

<sup>1</sup> Ann. der. Phys. 10, p. 360 (1903).

<sup>2</sup> Ann. der. Phys. 25, p. 205 (1908).

<sup>3</sup> " " 33, p. 1275 (1910).

<sup>4</sup> Wiener Berichte, 124, p. 577 (1915).

<sup>5</sup> Thesis Amsterdam (1914).

of methylene iodide and penta methylene, nitrobenzene and diisobutyl. Their observations were however restricted only to a short range of temperature above the critical temperature, for which the theory was intended. More recently Martin and Lehrman<sup>1</sup> made some interesting observations regarding the intensity and state of polarisation of some mixtures of liquids which are completely miscible at ordinary temperature, viz, carbon bisulphide and ether, benzene and normal hexane and normal hexane and cyclo hexane. As it was not the aim of the above authors to verify any theory but simply to observe the variation of intensity and polarisation of the scattered light for various concentrations of the mixtures, they chose some arbitrary pairs of liquids. As will be seen later from the theoretical part, partial vapour pressures and compressibilities of mixtures are necessary for the verification of the theory and unfortunately such data are not available for the pairs of liquids studied by Martin and Lehrman. V. S. Tamma, working at Calcutta, made a study of the scattering of light by mixtures of phenol and water for a range of 30°C above the critical solution temperature. He found the intensity of the scattered light to be very large and almost completely polarised in the immediate neighbourhood of the critical temperature and as the temperature is increased the intensity diminishes and the scattered light is less perfectly polarised. The present author<sup>2</sup> has studied the intensity of scattering and the state of polarisation of mixtures of carbon bisulphide and acetone. Following up this work the author has carried out a series of observations with mixtures of toluene and acetic acid at the room temperature and with mixtures of methyl alcohol and carbon bisulphide at temperatures both above and below the critical solution temperature, the results of which are now set out.

<sup>1</sup> Jour. Phys. Chem., 26, p. 75 (1922).

<sup>2</sup> Physical Review, July 1923. Hereafter this will be referred to as paper A.



## 2. *Technique of observation and measurement.*

The chief difficulty in the work is to prepare perfectly dust-free liquids. To achieve this end, slightly different forms of apparatus are used for the wholly miscible liquids and partially miscible ones. For the former, the mixtures are contained in cut glass bottles having flat sides and are rendered dust-free in the same manner as that described in paper A. Five different mixtures of toluene and acetic acid of different concentrations are prepared.

Though distillation in bottles is found to be very convenient for accurate measurements of intensity and polarisation at ordinary temperatures, at higher temperatures either the joints no longer remained tight with the result that leakage ensued or the bottles are not found to be strong enough to resist the large internal pressure. Thus for the study of scattering by mixtures of methyl alcohol and carbon bisulphide (a case of partially miscible liquids), at different temperatures the apparatus used is similar to that used by Raman and Seshagiri Rao.<sup>1</sup> The apparatus consists simply of two bulbs connected together containing the mixture and the air inside is exhausted to facilitate distillation. The liquid is distilled from one bulb to the other. After repeating the operation five or six times the bulb containing the liquid is sealed off. Three bulbs containing respectively 25, 50 and 75 per cent. of carbon bisulphide by volume are prepared.

For measurements of the intensity of scattered light, a second bottle containing toluene is used as a standard of comparison in all cases. The measurements are made in the same manner as described in paper A, the only difference being that in the case of mixtures of toluene and acetic acid, the two bottles are set closely side by side with a uniform film of glycerine between them, to ensure against any loss of light by reflection at the surfaces. To get more accurate results the bottles are interchanged, the relative intensity is noted

<sup>1</sup> Phil Mag., Mar. 1923, p. 625.

again and the mean value is then taken. In the case of mixtures of methyl alcohol and carbon bisulphide the bulb is immersed in a rectangular glass vessel having flat sides and containing clear distilled water. The glass sides are painted jet black outside, openings being left for admission and exit of the beam of light passing through the liquids. For the small thicknesses of the liquids used, the effect of the absorption of light is quite negligible. Indeed the colour of the tracks observed in the pure liquids and mixtures was found to be blue and no difficulty was experienced in making the intensity measurements. Care is taken to see (especially in the case of bulbs), that the liquids are exposed only for a short time to avoid any decomposition of the liquid when observations are taken.

Polarisation measurements are made as in the previous case by a double image prism and nicol. The double image prism gives two images of the track polarised respectively in horizontal and vertical planes. By rotating the prism the two images can be brought into a line. By rotating the nicol placed immediately behind the prism, two positions may be found in which the images appear of equal intensity. If  $2\theta$  be the angle between these positions of the nicol, then  $\gamma = \tan^2\theta$ , where  $\gamma$  is the ratio of the weak component to the strong.

### 3. *Results with wholly miscible liquids.*

The observed intensities for mixtures of toluene and acetic acid for different concentrations are given in the following table. As was stated before, Toluene is taken as the standard. The results refer to 30°C.

TABLE I.

Liquid	Toluene.	A.	B	C	D.	E	Acetic Acid.
Percentage volume of toluene	100	83.3	66.7	50	33.3	16.7	0
Observed intensity	1.0	1.05	1.0	1.0	0.78	0.70	0.50

For the same pair of liquids the ratios of the weak component to the strong, of polarisation are given in the following table:

TABLE II.

Liquid	Toluene.	A.	B.	O	D	E.	Acetic acid.
Percentage volume of toluene	100	83.3	66.7	50.0	33.3	16.7	0
0	33.3	34.3	31.6	30.2	29.7	32.8	37.4
100%	55	46.5	37.8	33.8	32.8	41.6	58.5

#### 4. Results with partially miscible Liquids.

The observed values of intensity for mixtures of methyl alcohol and carbon bisulphide for different concentrations and temperatures are given in the following table. In this case also toluene is taken as the standard. When the temperature is lowered the concentrations of the two layers in the bulbs alter. Intensities corresponding to these temperatures and concentrations are also included.

TABLE III.

Liquid.	Percentage volume of CS <sub>2</sub> .	OBSERVED INTENSITY.				
		<i>t</i> = 20°C	<i>t</i> = 30°C.	<i>t</i> = 40.5°C	<i>t</i> = 50°C	<i>t</i> = 60°C
CH <sub>3</sub> OH	0	0.08	0.08	0.1	3.1	0.33
A	25	0.72	0.74	0.92	1	1.1
B <sub>1</sub>	40	5.0	..	..	..	..
B <sub>2</sub>	48	...	8.5	..	..	..
B	50	...	..	23	14.5	6
C	75	..	...	80	16	9
CS <sub>2</sub>	100	1.5	1.5	1.75	1.75	2

For the same pair of liquids the polarisation measurements for different concentrations and temperatures are given in the following table :

TABLE IV.

Liquid.	Percentage volume of CS <sub>2</sub>	100 γ OBSERVED				
		$t = 20^{\circ}\text{C.}$	$t = 30^{\circ}\text{C.}$	$t = 40\ 5^{\circ}\text{C.}$	$t = 50^{\circ}\text{C.}$	$t = 60^{\circ}\text{C.}$
CH <sub>3</sub> OH	0	9 5	9	9	9	9
A	25	20 3	20 0	16 3	22 5	23
B <sub>1</sub>	40	10				
B <sub>2</sub>	48		6			
B	50			5 1	7	10
C	75			3	4 6	18
CS <sub>2</sub>	100	70	70	70	69	69

To have a clearer idea of the variation of intensity and polarisation with temperature the following tables are given for the scattering in the two layers of bulbs A and C which contain respectively 25 and 75 per cent. of carbon bisulphide. In the latter case, two layers were present till about 40°C, beyond which the boundary line disappeared :

## LIQUID A.

TABLE Va

Temperature	14	20	26	40 5	50	60
Intensity	0 71	0 72	0 74	0 92	1 00	1 33

## LIQUID C.

TABLE Vb.

Temperature in °C.	8	11	20	30	40 5	50	60
Intensity for upper layer	3	3 3	5	6 5	80	16	9
Intensity for lower layer	2	5	8	.			.

The above tables show very interesting variation of intensity with concentration and temperature. In the case of liquid A, where there is only a small percentage of  $\text{CS}_2$ , the mixture behaves like a pure liquid—the intensity increasing continuously with temperature. On the other hand liquid C which at the critical temperatures contains nearly 75 per cent. of  $\text{CS}_2$  behaves in quite a different way. The intensity increases with temperature for both the layers till the critical temperature is reached, when it becomes enormous and beyond which the intensity begins to diminish.

The polarisation measurements also show a similar interesting variation. For the first mixture A, the variation with temperature is very small but at the critical temperature however,  $\gamma$  is a minimum. For the other mixture, the scattered light is almost completely polarised at the critical point but for higher and lower temperatures, the polarisation tends to become more and more imperfect. This is shown by the following tables.

## LIQUID A.

TABLE VIa.

Temperature	10	15	20	30	40	50	60
100 $\gamma$	23	21.5	20.3	20	18.3	22.5	23

## LIQUID C.

TABLE VIb.

Temperature.	8	12.5	20	30	40.5	50	60
100 $\gamma$ for upper layer ...	24	20	10	6	3	4.6	10
100 $\gamma$ for lower layer ...	46	19	.	..	...	...	...

## PART II. THEORETICAL.

1. *Introduction.*

As was mentioned in the introduction to Part I, the theory of the opalescence of liquid mixtures near the critical solution temperature was supplied by Smoluchowski and Einstein. These authors regarded the opalescence in liquid mixtures as due to local fluctuations of composition and consequent optical inhomogeneity. Einstein's theory of liquid mixtures is intended to explain only the scattering of light in a small range of temperature above the critical solution temperature and is based on the following assumptions—that the liquids are incompressible, that their specific volumes are negligibly small in comparison with those of the saturated vapours emitted by them and that the latter can be treated as ideal gases; and on this basis he arrived at a formula for the opalescence of the mixture in terms of experimentally determinable magnitudes, namely, the variation of its refractive index and of the partial vapour pressure of its components with the alteration of concentration measured by the ratio of the mass of the second component to that of the first. This theory was verified for a small range above the critical temperature by Fürth and Zernike. The latter worked out also a theory based on statistical mechanics and arrived at a more general result, but in the end without making any calculations rejected the additional factors and finally arrived at Einstein's formula.

In a letter to *Nature*, C. V. Raman<sup>1</sup> drew attention to the limitation of Einstein's theory and showed that in the case of liquids which are completely miscible in all proportions at the ordinary temperature and in the case of partially miscible liquids at temperatures higher than the critical temperature, there are other factors, which must be taken into consideration, *e.g.*, molecular scattering of light due to density fluctuations of the liquid mixture and to the varying

<sup>1</sup> *Nature*, July 1922, p. 77

orientations of the anisotropic molecules. This latter factor accounts for the large amount of unpolarised light in liquids scattered transversely to the primary beam. A fuller theory taking these factors into account was given by Raman and Ramanathan,<sup>1</sup> who showed that the experimental results could thus be satisfactorily explained.

In this paper an attempt is made to develop a theory of scattering of light by liquid mixtures, on the lines of Ramanathan's work for the case of pure liquids.<sup>2</sup> In article 2, the medium is assumed to be continuous as in Einstein's treatment of the subject, but subject to local fluctuations of density and concentration of the mixture depending on the laws of statistical mechanics. Lorentz's electromagnetic treatment of the scattering of light in gases has been adopted and extended to the case of liquid mixtures. In article 3, the subject is treated from the molecular standpoint in the case when the molecules are isotropic and the formula of Raman and Ramanathan for scattering by liquid mixtures is deduced. In article 4, the treatment is extended to the case when the molecules are anisotropic and a formula is developed for the intensity of scattered light.

## 2. *Continuous medium theory.*

Let  $\epsilon$  be the value of the mean dielectric constant of a medium when the distribution of matter is uniform and  $\epsilon + \delta\epsilon$  its actual value at a volume element  $\delta v$ . In a liquid mixture, owing to thermal movements the density of the mixture taken as a whole and the concentration of one liquid in the other undergo incessant fluctuations; consequently the dielectric constant of the mixture also.

Using Heaviside's absolute units, the dielectric displacement

$$D = \epsilon E \quad \dots (1)$$

<sup>1</sup> Phil. Mag., Jan. 1923, p. 213.

<sup>2</sup> Proc. Ind. Assoc. Cult. Science, Vol. VIII, p. 1.

where  $E$  is the electric intensity. When the density and concentration of the mixture are uniform, there would be no scattering of light, for the disturbances from different elements would mutually cancel each other except in the direction of primary propagation. At a place where the dielectric constant is  $\epsilon + \delta\epsilon$  the dielectric displacement

$$D_1 = (\epsilon + \delta\epsilon)E \quad \dots (2)$$

The discontinuity of displacement can be annulled by introducing a supplementary electric intensity

$$F = -\frac{\delta\epsilon}{\epsilon} E \quad (3)$$

The scattering is thus identical with the radiation due to a system of electric intensities  $-F$  or  $\frac{\delta\epsilon}{\epsilon} E$  at the places where the dielectric constant differs from its mean value  $\epsilon$  by  $\delta\epsilon$ .

Suppose we have a volume element  $\delta v$  at the origin of co-ordinates where the dielectric constant is  $\epsilon + \delta\epsilon$ . When the linear dimensions of the element are small in comparison with the wave length, the amplitude of the disturbance from the element would be proportional to  $\frac{\delta\epsilon}{\epsilon} E \delta v$  and hence its energy is proportional to

$$\left(\frac{\delta\epsilon}{\epsilon}\right)^2 E^2 (\delta v)^2 \quad \dots (4)$$

In the case of scattering by a single volume element  $\delta v$

$$F = -\frac{\delta\epsilon}{\epsilon} E$$

and the ratio of the light radiated by the doublets to  $E^2$  the square of the amplitude can be shown to be

$$\frac{\sin^2 \theta}{r^2} \left(\frac{2\pi}{\lambda_1}\right)^4 \left(\frac{\delta\epsilon}{\epsilon}\right) \frac{(\delta v)^2}{16\pi^2} \quad \dots (5)$$



where  $\lambda_1$  is the wave length of the incident vibration in the medium and  $\theta$  is the angle between the direction of the ray and axis of Z (the direction of the applied electric intensity).

Let us now consider the scattering produced by the accidental deviations of density and concentration in an extended volume. Let us take the X-axis to be the direction of the primary beam. The density and concentration deviations would change both in magnitude as well as in position in a perfectly arbitrary manner and there would be no co ordination of phase between the vibrations scattered by the various elements. As a consequence, over any finite interval of time, the energies and not the amplitudes of the scattered radiations from the different elements of volume would be additive. If  $\delta\rho$  and  $\delta k$  denote the deviations of density and concentration from their mean values  $\rho_0$  and  $k_0$  in a volume element  $\delta v$  then we can easily show by Boltzmann's principle of entropy probability that the mean squares of deviations of density and concentration are given by <sup>1</sup>

$$(\overline{\delta\rho})^2 = \frac{RT\beta}{N\delta v} \rho_0^2 \quad \dots (6)$$

$$(\overline{\delta k})^2 = \frac{1}{\pi^2 N\delta v} \frac{M_2}{m_1} \frac{\partial \log p_2}{\partial k} \quad \dots (7)$$

$$\text{and} \quad \overline{\delta\rho} \quad \overline{\delta k} = 0 \quad \dots (8)$$

where R is the gas constant, T is the absolute temperature,  $M_2$  is the molecular weight of the second component in the gaseous phase,  $m_1$  mass of the first component in unit volume of the mixture,  $p_2$  is the partial vapour pressure of the second component,  $\phi$  is the compressibility of the mixture.

Now

$$\delta\epsilon = \frac{\partial\epsilon}{\partial k} \delta k + \frac{\partial\epsilon}{\partial\rho} \delta\rho$$

$$(\overline{\delta\epsilon})^2 = \left( \frac{\partial\epsilon}{\partial k} \right)^2 (\overline{\delta k})^2 + \left( \frac{\partial\epsilon}{\partial\rho} \right)^2 (\overline{\delta\rho})^2 \quad \dots (9)$$

<sup>1</sup> Einstein Ann. der Phys., Vol. 33, 1910, p. 1275, also C. V. Raman and Ramanathan, Phil. Mag., Jan. 1923, p. 213.

The relation between density and dielectric constant is given by Lorentz's formula, considering a mixture as a whole,

$$\frac{\epsilon-1}{\epsilon+2} \cdot \frac{1}{\rho_0} = \text{constant}$$

Hence

$$\frac{\partial \epsilon}{\partial \rho} = \frac{(\epsilon-1)(\epsilon+2)}{3\rho_0}$$

$$\left( \frac{\partial \epsilon}{\partial \rho} \right)^2 (\delta \rho)^2 = \frac{(\epsilon-1)^2 (\epsilon+2)^2}{9\rho_0^2}$$

and by (6)

$$= \frac{(\epsilon-1)^2 (\epsilon+2)^2}{9} \frac{RT\beta}{N\delta v}$$

Substituting in (5) the value of  $(\delta \epsilon)^2$  from (9) with the help of (6) and (7), we get for the ratio of the average intensity of the scattered radiation to that of the incident

$$\left[ \frac{\pi^2}{9} RT\beta (\epsilon-1)^2 (\epsilon+2)^2 + \frac{M_2 (\partial \epsilon / \partial k)^2}{m_1 \partial \log p_2 / \partial k} \right] \frac{\sin^2 \theta}{N\epsilon \lambda_1^4} \delta v$$

Since the radiations from different volume elements are additive the above becomes

$$\left[ \frac{\pi^2}{9} RT\beta (\epsilon-1)^2 (\epsilon+2)^2 + M_2 \frac{1}{m_1} \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k} \right] \frac{\sin^2 \theta}{N\lambda^4} \dots (11)$$

per unit volume where  $\lambda$  is the wave length of the incident vibration in vacuo.

In a direction at right angles to the primary incident beam, the above expression becomes

$$\left[ \frac{\pi^2}{9} RT\beta (\epsilon-1)^2 (\epsilon+2)^2 + \frac{M_2}{m_1} \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k} \right] \frac{1}{N\lambda^4 r^2}$$

### 3. *The Electron theory of Scattering by isotropic molecules.*

The problem of scattering of light can also be considered from a molecular standpoint. In this case the electromagnetic waves falling on a molecule produce a displacement of the electrons in that molecule. This is equivalent to creating an oscillating electric doublet in each molecule with a period the same as that of the waves. We shall however exclude the case of electrons having a natural period equal to the period of the incident waves. For isotropic molecules the axes of the doublets coincide in direction with that of the external electric force, but for anisotropic molecules the displacements of the electrons are not in general in that direction. The total effect may, however, be taken as equivalent to creating of three doublets with their axes along the three principal directions in each molecule. The field to which any molecule is subject is the resultant of that due to the incident wave and that due to the polarisation of the neighbouring molecules. In the following paragraphs, a method is developed from the molecular standpoint.

Consider a plane polarised wave travelling in the direction  $Ox$ . Let  $Z$  be the electric intensity in the wave parallel to  $Oz$  and proportional to  $\cos pt$ . Under the influence of the incident wave each molecule behaves as a doublet with its axis parallel to  $Oz$ . Let  $A_1$  be the moment induced in a molecule of the first component when it is placed in a field of unit intensity. Let  $A_2$  be the value for the second component of the mixture. Let  $n$  be the total number of molecules in a unit volume of the mixture of which  $n_1$  are of the first component and  $n_2$  of the second. Let  $M_1$  and  $M_2$  be the electrical moments of the doublets of the two components. The total intensity at any point in the medium is

$$Z + \frac{4\pi}{3} n_1 M_1 + \frac{4\pi}{3} n_2 M_2$$

and

$$\begin{aligned}
 M_1 &= A_1 \left( Z + \frac{4\pi}{3} n_1 M_1 + \frac{4\pi}{3} n_2 M_2^* \right) \\
 &= \frac{A_1 Z}{1 - \frac{4\pi}{3} n_1 A_1} + \frac{A_1 \frac{4\pi}{3} n_2 M_2}{1 - \frac{4\pi}{3} n_1 A_1} \quad \dots (12)
 \end{aligned}$$

Similarly

$$M_2 = \frac{A_2 Z}{1 - \frac{4\pi}{3} n_2 A_2} + \frac{A_2 \frac{4\pi}{3} n_1 M_1}{1 - \frac{4\pi}{3} n_2 A_2} \quad \dots (12a)$$

The above equations can be written as

$$\begin{aligned}
 M_1 &= \frac{A_1 Z}{1 - \frac{4\pi}{3} n_1 A_1} + \frac{\frac{4\pi}{3} n_2 A_1 A_2 Z}{(1 - \frac{4\pi}{3} n_1 A_1)(1 - \frac{4\pi}{3} n_1 A_1 - \frac{4\pi}{3} n_2 A_2)} \\
 &\quad \frac{A_1 Z}{1 - \frac{4\pi}{3} n_1 A_1 - \frac{4\pi}{3} n_2 A_2} \quad \dots (13)
 \end{aligned}$$

and similarly

$$M_2 = \frac{A_2 Z}{1 - \frac{4\pi}{3} n_1 A_1 - \frac{4\pi}{3} n_2 A_2} \quad \dots (13a)$$

Now  $\epsilon_1$  the square of the refractive index of the first component for waves of frequency  $p/2\pi$  is given by

$$\frac{\epsilon_1 - 1}{\epsilon_1 + 2} = \frac{4\pi}{3} n'_1 A_1 \quad \dots (14)$$

where  $n'_1$  is the number of molecules in a unit volume of the first component. For the second component we have similarly

$$\frac{\epsilon_2 - 1}{\epsilon_2 + 2} = \frac{4\pi}{3} n'_2 A_2 \quad \dots (14a)$$

where  $n'_2$  is the number of molecules contained in a unit volume of the second component and  $\epsilon_2$  the square of the refractive index of the second component.

Remembering that

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\epsilon_1-1}{\epsilon_1+2} \cdot \frac{n_1}{n'_1} + \frac{\epsilon_2-1}{\epsilon_2+2} \cdot \frac{n_2}{n'_2}$$

where  $\epsilon$  is the square of the refractive index of the mixture the expressions for  $M_1$  and  $M_2$  become after some simplification

$$M_1 = A_1 Z \cdot \frac{\epsilon+2}{3} \quad \dots \quad (15)$$

and

$$M_2 = A_2 Z \cdot \frac{\epsilon+2}{3} \quad \dots \quad (15a)$$

A vibrating electric doublet radiates out energy. According to Hertz's well-known solution, the electric intensity at time  $t - \frac{r}{c}$  at a point  $r$  distant (great in comparison with  $\lambda$ ) from the doublet of moment  $M_1$ , is

$$\frac{p^2}{c^2 r} M_1 \Big|_{t-\frac{r}{c}} \sin \theta \quad \dots \quad (16)$$

where  $c$  is the velocity of light in vacuo,  $\theta$  is the angle between  $Oz$  and the direction of the ray and  $M_1 \Big|_{t-\frac{r}{c}}$  stands for the value of the moment at time

For a medium containing molecules which are uniformly distributed, the effect due to a volume whose dimensions are large compared with  $\lambda$ , vanishes in all directions except in the direction of primary propagation where the secondary waves from the different molecules in the wave front combine with the original wave and give rise to a plane wave moving with an altered velocity. In any medium, containing a mixture of

liquids, however, owing to thermal movements of the molecules, and the consequent fluctuations of density and concentration at any point, there is a finite radiation of energy in all directions. If  $n$  represents the average number of molecules per unit volume in a volume element  $\delta v$  and  $\overline{\delta n^2}$  the mean square of the deviations of that number, then we have

$$\frac{\overline{\delta n^2}}{n} = \frac{RT\beta}{N\delta v} \quad \dots (17)$$

If  $k$  is the concentration of the mixture, the mean square of the deviation of that quantity is given by

$$(\overline{\delta k})^2 = \frac{M_1}{\pi^2 N \delta v} \frac{1}{m_1 \partial \log p_1 / \partial k} \quad \dots (18)$$

we have also the relation

$$(\delta k) (\delta n) = 0 \quad \dots (19)$$

Consider a volume element  $\delta v$  small in comparison with the wave length, but large compared with the dimensions of a molecule. Let  $n$  be the average number of molecules present per unit volume in  $\delta v$  of which  $n_1$  are of the first component and  $n_2$  are of the second, so that  $n_1 + n_2 = n$ . If  $\rho$  is the density of the mixture, then  $n$  is proportional to  $\rho$ . To calculate the intensity of light scattered by the molecules in the volume  $\delta v$ , we have to take two factors into consideration—one is due to the variation of  $n$  or density  $\rho$  consequent on the variation of  $n_1$  and  $n_2$ , keeping the proportion of  $n_2$  to  $n_1$ , i.e., the concentration  $k$  fixed. This part gives the scattering due to fluctuations of the density of the mixture taken as a single liquid. The other is due to the variation of the proportion of  $n_2$  to  $n_1$ , keeping the pressure constant. This part accounts for the scattering due to fluctuations in concentration.

The electric vector at P due to scattering by the molecules contained in a volume  $\delta v$  is given by

$$\begin{aligned} Z' &= \frac{\rho^2}{c^2 r} \sin \theta \delta v [(M_1 + \delta M_1)(n_1 + \delta n_1) - M_1 n_1 \\ &\quad + (M_2 + \delta M_2)(n_2 + \delta n_2) - M_2 n_2 + \frac{\partial}{\partial k} (M_1 n_1 + M_2 n_2) \delta k] \\ &= \frac{\rho^2}{c^2 r} \sin \theta \delta v [M_1 \delta n_1 + n_1 \delta M_1 + M_2 \delta n_2 + n_2 \delta M_2 \\ &\quad + \frac{\partial}{\partial k} (M_1 n_1 + M_2 n_2) \delta k] \end{aligned}$$

Since  $n_1 M_1 + n_2 M_2$  is the total polarisation at the point O, it is proportional to  $(\epsilon - 1)/4\pi$  and hence

$$\frac{\partial}{\partial k} (n_1 M_1 + n_2 M_2) = \frac{Z}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k$$

The above expression therefore becomes

$$= \frac{\rho^2}{c^2 r} \sin \theta \delta v \left[ M_1 \delta n_1 + \delta M_1 n_1 + n_2 \delta M_2 + M_2 \delta n_2 + \frac{Z}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right] \quad \dots (20)$$

To evaluate the expression  $M_1 \delta n_1 + n_1 \delta M_1 + M_2 \delta n_2 + n_2 \delta M_2$ , we have the relation—

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} (n_1 A_1 + n_2 A_2) \quad \dots (21)$$

Now differentiating (21), we get after some simplification

$$\frac{4\pi}{3} (A_1 \delta n_1 + A_2 \delta n_2) = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{\delta n}{n} \quad \dots (22)$$

From (15) and (21), we get in a similar manner

$$\begin{aligned} \delta M_1 &= A_1 Z \left( \frac{\epsilon + 2}{3} \right)^2 \left[ \frac{4\pi}{3} A_1 \delta n_1 + \frac{4\pi}{3} A_2 \delta n_2 \right] \\ &= A_1 Z \frac{(\epsilon - 1)(\epsilon + 2)}{9} \frac{\delta n}{n} \quad \dots (23) \end{aligned}$$

Similarly

$$\delta M_2 = A_2 Z \frac{(\epsilon-1)(\epsilon+2)}{9} \frac{\delta n}{n} \quad \dots (23a)$$

Substituting the values of  $\delta M_1$  and  $\delta M_2$  given by equations (23) and (23a) and taking the values of  $M_1$  and  $M_2$  given by relations (15) and (15a), we get with the help of equations (21) and (22).

$$M_1 \delta n_1 + n_1 \delta M_1 + n_2 \delta M_2 + M_2 \delta n_2 = Z \frac{(\epsilon-1)(\epsilon+2)}{12\pi} \frac{\delta n}{n} \quad \dots (24)$$

Substituting the above value in equation (20), we get for the electric intensity at  $\rho$  due to scattering by the molecules contained in volume  $\delta v$

$$E = \frac{p^2 z}{c^2 r} \sin \theta \delta v \left[ \frac{(\epsilon-1)(\epsilon+2)}{12\pi} \frac{\delta n}{n} + \frac{1}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right] \quad \dots (25)$$

The energy being proportional to  $E^2$  is given by

$$E^2 = \frac{p^4 Z^2}{c^4 r^2} \sin^2 \theta (\delta v)^2 \left[ \frac{(\epsilon-1)(\epsilon+2)}{12\pi} \frac{\delta n}{n} + \frac{1}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right]^2 \quad \dots (26)$$

Since  $\delta n$  and  $\delta k$  vary from instant to instant according to the laws of chance the average expectancy of  $E^2$  over a sufficiently long interval of time is

$$E^2 = \frac{p^4 Z^2}{c^4 r^2} \sin^2 \theta \left[ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \frac{\overline{\delta n^2}}{n^2} + \frac{1}{16\pi^2} \left( \frac{\partial \epsilon}{\partial k} \right)^2 (\delta k)^2 \right] (\delta v)^2$$

By (17) and (18), and remembering that  $p/c = 2\pi/\lambda$  we arrive at the formula (11) for a volume  $V$ .

#### 4. Scattering by anisotropic molecules.

When the arrangement of the electrons in a molecule is symmetrical, then the displacement of the electrons will be in the direction of the applied electric force and independent of



the direction. If it is unsymmetrical the displacement may not be in the direction of the force and scattered light will not be completely polarised. In this article the anisotropy of the molecules is taken into consideration in calculating the scattering of light by binary liquid mixtures.

Let  $O\xi_1, O\eta_1, O\zeta_1$ , denote the three principal directions in a molecule of the first component at right angles to each other such that the electrons can be displaced along any of them, without causing displacement along the other two. Similarly let  $O\xi_2, O\eta_2, O\zeta_2$ , denote the three principal directions of a molecule of the second component. Let  $Ox, Oy$ , and  $Oz$  be three fixed axes. Let  $A_1, B_1, C_1$ , be the moments induced in a molecule of the first component when placed in a field of unit intensity parallel to  $O\xi_1, O\eta_1, O\zeta_1$  respectively. Let  $A_2, B_2, C_2$  be the corresponding values for the second component. As before let  $Oz$  be the direction of the incident polarised plane wave and  $Z$  the electric intensity along  $Oz$ . The molecules being anisotropic, there will be components both along the  $x$  and  $y$  axes. But when the axes of the molecules are oriented at random the mean values of polarisation parallel to  $x$  and  $y$  axes vanish. But the value along the  $z$  axis which is

$$\frac{4\pi}{3} n_1 \overline{M}_z + \frac{4\pi}{3} n_2 \overline{M}'_z,$$

is not zero, as  $\overline{M}_z$  and  $\overline{M}'_z$  which are the moments of each of the two components, can have only positive values.  $n_1$  and  $n_2$  are the number of molecules of the two components in unit volume.

The effect of polarisation of the surrounding molecules is then to produce an additional field of

$$\frac{4\pi}{3} n_1 \overline{M}_z + \frac{4\pi}{3} n_2 \overline{M}'_z.$$

The resultant electric field is therefore

$$Z + \frac{4\pi}{3} n_1 \overline{M}_z + \frac{4\pi}{3} n_2 \overline{M}'_z.$$

To calculate  $\bar{M}_z$ , we note that if the molecules are oriented at random

$$\begin{aligned}\bar{M}_z &= \frac{A_1 + B_1 + C_1}{3} \left[ Z + \frac{4\pi}{3} n_1 \bar{M}_z + \frac{4\pi}{3} n_2 \bar{M}' \right] \\ &= \frac{A_1 + B_1 + C_1}{3} \cdot \frac{\epsilon + 2}{3} Z \quad \dots (27)\end{aligned}$$

as in the previous section.

$$M'_z = \frac{A_2 + B_2 + C_2}{3} \cdot \frac{\epsilon + 2}{3} Z \quad \dots (27a)$$

and

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \left[ \frac{A_1 + B_1 + C_1}{3} n_1 + \frac{A_2 + B_2 + C_2}{3} n_2 \right] \quad \dots (28)$$

If  $\theta, \phi, \psi$  are the Eulerian co-ordinates defining a molecule of the first component with respect to the fixed axes, we have for the moments induced in the molecule parallel to  $O\xi_1, O\eta_1, O\zeta_1$ ,

$$-A_1 Z \frac{\epsilon + 2}{3} \sin \theta \cos \phi, \quad B_1 Z \frac{\epsilon + 2}{3} \sin \theta \sin \phi, \quad C_1 Z \frac{\epsilon + 2}{3} \cos \theta \quad \dots (29)$$

When these are resolved along  $Ox, Oy, Oz$  the components are

$$\begin{aligned}M_x &= Z \cdot \frac{\epsilon + 2}{3} [\sin \theta \cos \theta \cos \psi (C_1 - A_1 \cos^2 \phi - B_1 \sin^2 \phi) \\ &\quad + (A_1 - B_1) \sin \theta \sin \psi \sin \phi \cos \phi] \quad \dots (30)\end{aligned}$$

$$\begin{aligned}M_y &= Z \cdot \frac{\epsilon + 2}{3} [\sin \theta \cos \theta \sin \psi (C_1 - A_1 \cos^2 \phi - B_1 \sin^2 \phi) \\ &\quad + (A_1 - B_1) \sin \theta \cos \psi \sin \phi \cos \phi] \quad \dots (31)\end{aligned}$$

$$M_z = Z \cdot \frac{\epsilon + 2}{3} [C_1 \cos^2 \theta + B_1 \sin^2 \theta \sin^2 \phi + A_1 \sin^2 \theta \cos^2 \phi] \quad \dots (32)$$

which for shortness, we may write

$$Z \cdot \frac{\epsilon+2}{3} \mathcal{L}_1, \quad Z \cdot \frac{\epsilon+2}{3} \mathcal{L}_2, \quad Z \cdot \frac{\epsilon+2}{3} \mathcal{L}_3$$

Similarly if  $\theta'$ ,  $\phi'$ ,  $\psi'$  are the values of  $\theta$ ,  $\phi$  and  $\psi$  for the second component, we get

$$M'_1 = Z \cdot \frac{\epsilon+2}{3} \mathcal{L}'_1, \quad \dots \quad (30a)$$

$$M'_2 = Z \cdot \frac{\epsilon+2}{3} \mathcal{L}'_2, \quad \dots \quad (31a)$$

$$M'_3 = Z \cdot \frac{\epsilon+2}{3} \mathcal{L}'_3, \quad \dots \quad (32a)$$

where  $\mathcal{L}'_1$ ,  $\mathcal{L}'_2$  and  $\mathcal{L}'_3$  are the expressions for  $\mathcal{L}_1$ ,  $\mathcal{L}_2$ ,  $\mathcal{L}_3$  with  $\theta'$ ,  $\phi'$  and  $\psi'$  written for  $\theta$ ,  $\phi$  and  $\psi$  respectively and  $A_2$ ,  $B_2$ ,  $C_2$  written for  $A_1$ ,  $B_1$ ,  $C_1$  respectively.

To calculate the intensity of light scattered in any direction from a unit volume, we have to add together the contributions from all the molecules contained in it, due regard being paid to the phases of the waves scattered. In the case of isotropic molecules the induced moments are all parallel to the external field and the direction of vibration in the scattered light is parallel to that in the incident. With anisotropic molecules, however, the scattered light has also in general, vibrations perpendicular to those in the incident. In a binary liquid mixture containing isotropic molecules, the scattering can be supposed to arise from density and concentration fluctuations and in a medium containing anisotropic molecules, we have in addition scattering due to random character of the orientations of the molecules. In calculating the intensity of light scattered by a mixture of anisotropic molecules, we may suppose them to be replaced by isotropic molecules, having the same induced moments as the

average moment of the anisotropic molecules and proceed to calculate the intensity of scattered light due to fluctuations of density and concentration as in the previous section.

Thus in the case of a unit volume of the mixture containing  $n_1$  molecules of the first component and  $n_2$  of the second the sum of the induced moments in the direction of the  $x$ -axis is given by

$$\frac{4\pi}{3} (n_1 \bar{M}_x + n_2 \bar{M}'_x)$$

where  $\bar{M}_x$  and  $\bar{M}'_x$  are the mean values for the  $x$ -component of the moments of the two kinds of molecules. From (30) and (30a), the mean values will be zero. Similarly the  $y$ -component is zero and the  $z$ -component is given by

$$\frac{4\pi}{3} (\bar{M}_z n_1 + \bar{M}'_z n_2),$$

i.e.,

$$\frac{4\pi}{3} \frac{\epsilon + 2}{9} [(A_1 + B_1 + C_1)n_1 + (A_2 + B_2 + C_2)n_2]$$

We can now proceed exactly as in the case of isotropic molecules, to find the intensity of light scattered by a unit volume of the mixture due to density and concentration fluctuations, for which we get similar expressions as in the previous section.

Actually, however, each anisotropic molecule has in any direction a moment different from the average value on account of its varying orientation, and the fluctuation of the value of the moment from its mean value gives rise to an additional scattering. Thus for a unit volume, the fluctuations in moments from their average values in the direction are given by

$$M_x n_1 + M'_x n_2, \quad M_y n_1 + M'_y n_2,$$

and

$$\frac{\epsilon + 2}{3} \left[ \left( \frac{A_1 + B_1 + C_1}{3} - \bar{L}_x \right) n_1 + \left( \frac{A_2 + B_2 + C_2}{3} - \bar{L}'_x \right) n_2 \right]$$

We shall now proceed to calculate the light scattered by a unit volume of the mixture arising out of the two ways mentioned above.

At a point on the  $y$ -axis distant  $r$  from O, the  $x$ -component of the electric vector due to scattering from a molecule at O is

$$\frac{p^2}{c^2 r} M_x$$

The total effect of all the molecules contained in a small volume element  $\delta v$ , which is small compared with the wavelength but large compared with the linear dimensions of the molecule is given by

$$X' = \frac{p^2}{c^2 r} \sum M_x$$

Since  $\delta v$  contains a large number of molecules with their orientations at random  $\sum M_x$  would in general be small, as positive and negative values of  $M_x$  are equally probable. Indeed when the number of molecules is large the mean value would be zero. But the value of  $(\sum M_x)^2$  however when  $M_x$  is as often positive as negative is, as the late Lord Rayleigh<sup>1</sup> has shown,

$$(\sum M_x)^2 = n \cdot \overline{M_x^2} \delta v \quad \dots (33)$$

where  $n\delta v$  is the number of molecules in  $\delta v$ . For a binary mixture containing  $n_1\delta v$  and  $n_2\delta v$  molecules of the two components the average expectation  $X'^2$  is

$$X'^2 = \frac{p^4}{c^4 r^2} (\overline{M_x^2} n_1 + \overline{M_x^2} n_2) \delta v$$

<sup>1</sup> Theory of Sound, Vol. 1, Art. 42a.

Substituting the values of  $M_z$  and  $M'_z$  given by (30) and (30a) and averaging over all orientations of the molecules

$$\begin{aligned}\overline{X'} &= \frac{P^2 Z^2}{c^2 r^2} \left( \frac{\epsilon+2}{3} \right)^2 \cdot \frac{1}{15} [(A_1^2 + B_1^2 + C_1^2 - A_1 B_1 - B_1 C_1 - C_1 A_1) n_1 \\ &\quad + (A_2^2 + B_2^2 + C_2^2 - A_2 B_2 - B_2 C_2 - C_2 A_2) n_2] \delta v \quad \dots (34) \\ &= \frac{P^2 Z^2}{c^2 r^2} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2)\end{aligned}$$

where

$$f_1 = \frac{1}{15} (A_1^2 + B_1^2 + C_1^2 - A_1 B_1 - B_1 C_1 - C_1 A_1)$$

and

$$f_2 = \frac{1}{15} (A_2^2 + B_2^2 + C_2^2 - A_2 B_2 - B_2 C_2 - C_2 A_2)$$

For a volume  $V$ ,

$$\overline{X'} = \frac{P^2 Z^2}{c^2 r^2} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) V \quad \dots (35)$$

In the case of the  $z$ -component of the electric intensity at  $P$  in the waves scattered from a volume element  $\delta v$ , we have, as seen above, to take into consideration two parts—one, the scattering due to the molecules, when they are replaced by isotropic molecules having the same average moment as the anisotropic molecules. This gives, as in the previous section, scattering due to density and concentration fluctuations. The other is due to fluctuation of the moments of the anisotropic molecules on account of their varying orientations. The second part as in the case of the  $x$ -component of the electric intensity is proportional to the number of molecules and the first is proportional to the square of that number.

The first part of the square of the  $z$ -component of the electric vector at P in the waves scattered from a volume  $\delta v$  at O, is given as in the case of isotropic molecules, by

$$\begin{aligned}
 P^2 Z^2 (\delta v)^2 & \cdot \left\{ \left[ \delta(M, n_1 + M', n_2) \right]^2 + \left[ \frac{\partial}{\partial k} (M, n_1 + M', n_2) \delta k \right]^2 \right\} \\
 &= \frac{P^2 Z^2}{c^4 r^4} (\delta v)^2 \left[ \left( \frac{\epsilon+2}{3} \right)^2 (M, \delta n_1 + M', \delta n_2)^2 + \left( \frac{1}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right)^2 \right] \\
 &= \frac{P^2 Z^2}{c^4 r^4} (\delta v)^2 \left[ \frac{(\epsilon-1)^2 (\epsilon+2)^2}{144\pi^2} \frac{\delta n^2}{n^2} + \frac{1}{16\pi^2} \left( \frac{\partial \epsilon}{\partial k} \delta k \right)^2 \right] \quad \dots (36)
 \end{aligned}$$

The second part for a volume  $\delta v$  is given by

$$\begin{aligned}
 \frac{P^2 Z^2}{c^4 r^4} \left( \frac{\epsilon+2}{3} \right)^2 & \left\{ \left( \frac{A_1 + B_1 + C_1}{3} - L_1 \right) n_1 \right. \\
 & \left. + \left( \frac{A_2 + B_2 + C_2}{3} - L'_1 \right) n_2 \right\} \delta v
 \end{aligned}$$

This reduces for all orientations to

$$\cdot \frac{P^2 Z^2}{c^4 r^4} \left( \frac{\epsilon+2}{3} \right)^2 \cdot \frac{4}{3} (f_1 n_1 + f_2 n_2) \delta v \quad \dots (37)$$

Hence the total value of the square of the  $z$ -component of the electric vector is given by

$$\begin{aligned}
 \overline{Z^2} &= \frac{P^2 Z^2}{c^4 r^4} \left[ \left\{ \frac{(\epsilon-1)^2 (\epsilon+2)^2}{144\pi^2} \frac{\overline{\delta n^2}}{n^2} + \frac{1}{16\pi^2} \left( \frac{\partial \epsilon}{\partial k} \right)^2 (\overline{\delta k})^2 \right\} (\delta v)^2 \right. \\
 & \left. + \frac{4}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) \delta v \right] \quad \dots (38)
 \end{aligned}$$

Substituting the values of  $(\delta n)^2$  and  $(\delta k)^2$  from (26) and (27) we get

$$\begin{aligned} \overline{Z}^2 = \frac{P \cdot Z^2}{c^2 r^2} \left[ \left\{ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2}{m_1} \cdot \frac{(\partial \epsilon / \partial k)^2}{N \partial \log p_2 / \partial k} \right\} \right. \\ \left. + \frac{4}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) \right] \delta v \end{aligned}$$

For a volume V,

$$\begin{aligned} \overline{Z}^2 = \frac{P \cdot Z^2}{c^2 r^2} \left[ \left\{ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2}{m_1} \cdot \frac{(\partial \epsilon / \partial k)^2}{N \partial \log p_2 / \partial k} \right\} \right. \\ \left. + \frac{4}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) \right] V. \quad \dots (39) \end{aligned}$$

When the incident light is unpolarised the ratio of the two components is given by

$$\begin{aligned} \gamma = \frac{2 \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2)}{\frac{7}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) + \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2}{N m_1} \cdot \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k}} \quad \dots (40) \end{aligned}$$

The total intensity of the scattered light for a volume V is given by

$$\begin{aligned} \frac{P \cdot Z^2}{c^2 r^2} V \left\{ \frac{13}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) + \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} \right. \\ \left. + \frac{1}{16\pi^2} \cdot \frac{M_2}{N m_1} \cdot \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k} \right\} \\ = \frac{P \cdot Z^2}{c^2 r^2} V \left\{ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2}{N m_1} \cdot \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k} \right\} \end{aligned}$$



$$\left[ 1 + \frac{\frac{13}{3} \cdot (f_1 n_1 + f_2 n_2)}{\frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2(\partial \epsilon / \partial k)^2}{N m_1 \partial \log p_2 / \partial k}} \right]$$

This reduces after a little simplification to

$$V \cdot \left\{ \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (\epsilon-1)^2(\epsilon+2)^2 + \frac{M_2(\partial \epsilon / \partial k)^2}{N\lambda^4 m_1 \partial \log p_2 / \partial k} \right\} \left[ \frac{6(1+\gamma)}{6-7\gamma} \right] \quad \dots (41)$$

where  $\lambda$  is the wave-length in vacuo. The above formula can be seen to be the same expression as for the isotropic molecules multiplied by the Cabannes' factor.

In the case of a single substance the above reduces to

$$\frac{RT\beta}{N\lambda^4} (\epsilon-1)^2(\epsilon+2)^2 \cdot \frac{6(1+\gamma)}{6-7\gamma} \quad \dots (41a)$$

### PART III.

#### *Comparison of Theory and Experiment.*

##### 1. INTENSITY.

The intensity of light scattered by mixtures of toluene and acetic acid at the room temperature will be considered. Toluene is taken as the first component and acetic acid as the second. In calculating the density and concentration scatterings the common multiplying factor  $1/N\lambda^4$  is omitted. The compressibility data are taken from Cohen and Schut's *Piezo Chemie*. The compressibilities for different concentrations are given in the following table.

TABLE VII.

Liquid.	Toluene	K=0.197	K=0.575	K=1.651	K=3.03	Acetic acid
$\beta \cdot 10^6$	91.4	82	87	85	89	96

The variation of refractive index with concentration is calculated for the F-line from the following well-known formula

$$\frac{\epsilon-1}{\epsilon+2} \cdot \frac{1}{\rho} = \frac{\epsilon_1-1}{\epsilon_1+2} \cdot \frac{f_1}{\rho_1} + \frac{\epsilon_2-1}{\epsilon_2+2} \cdot \frac{f_2}{\rho_2} \quad \dots (42)$$

where  $\epsilon$ ,  $\epsilon_1$ ,  $\epsilon_2$  are respectively the refractive indices of the mixture and the two components,  $\rho$ ,  $\rho_1$ ,  $\rho_2$  are respectively the densities of the mixtures and the two components,  $f_1$  and  $f_2$  are the fractions of the masses of each of the two components in the total mass of the mixture. The values of  $\epsilon$  for different concentrations are given in the table VIII.

TABLE VIII.

K	Toluene	0.11	0.25	0.43	0.67	1.0	1.25	2.33	4.0	9.0	Acetic acid
.	2.281	2.247	2.210	2.172	2.135	2.096	2.058	2.018	1.978	1.936	1.894

Though the incident light is not homogeneous, as we are concerned only with the ratios and not with the absolute values, we will not be far from right if we take the refractive indices corresponding to the F line as representative of the whole. From Tables VII and VIII the compressibilities and refractive indices for the required concentrations are obtained by interpolation. Knowing  $R$  to be equal to  $83.15 \times 10^6$  C.G.S. units, the values of  $\Omega_1$ ,  $N\lambda^4$  are calculated. where

$$\Omega_1 = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} \cdot (\epsilon-1)^2 (\epsilon+2)^2.$$

For calculating the concentration scattering, the variation of  $\log p_2$  where  $p_2$  is the partial vapour pressure of the second component (acetic acid in this case), with concentration is given in the following table :

TABLE IX.

K	0	0.03	0.069	0.135	0.206	0.318	0.451	0.567	0.690	0.971	1.437	2.171	4.568	Acetic acid
$\log p_2 - 2$	0	0.542	1.115	1.537	1.754	1.936	2.057	2.125	2.177	2.259	2.322	2.405	2.489	2.610

The variation of  $\epsilon$  with  $k$  is given in the Table VIII. The values of  $\delta \log p_2 / \delta k$  are found by the usual method after drawing a graph with  $k$  as abscissa and  $\log p_2$  as ordinate. In a similar manner,  $\partial \epsilon / \partial k$  is found from another graph. Then the values of  $\Omega_2$ ,  $N\lambda^4$  are calculated,

$$\text{where} \quad \Omega_2 = \frac{M_2}{2N\lambda^4 m_1} \left[ \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k} \right]$$

The orientation scattering is first calculated for toluene and acetic acid from equation (4) of paper A after knowing the ratio of the two components of polarisation from the observed values. From (35) the orientation scattering for any mixture divided by  $\left(\frac{+1}{3}\right)^2$  is proportional to the number of molecules of each component, the variations of  $4\Omega_2 / \left(\frac{+2}{3}\right)^2$  with  $k$  will be linear and the orientation scattering is easily calculated. The following table gives the calculated and observed intensities for the transversely scattered light :

TABLE X.

Liquid	Percentage Volume of CS <sub>2</sub>	Concentration K	$\Omega_1 N\lambda^4$	$\Omega_2 N\lambda^4$	$4\Omega_2 N\lambda^4$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						$(\Omega_1 + \Omega_2 + 4\Omega_2) N\lambda^4$	According to (41)	Calculated	E & R <sup>1</sup>	J.O.K. <sup>2</sup> Observed.
Toluene	100		37.2	0	91	128	143.5	1.0	1.0	1.0
A	83.3	0.24	28.9	20	82	131	157	1.03	1.11	1.05
B	66.7	0.61	26.8	30	73	131	141	1.04	1.0	1.0
C	50.0	1.21	22.7	38	65	126	135	1.0	0.91	1.0
D	33.3	2.43	19.5	34.6	58	103	114	0.81	0.8	0.78
E	16.7	6.07	17.7	14.9	51	84	90	0.65	0.63	0.70
Acetic acid	0		15.7	0	44	60	78.4	0.47	0.55	0.5

<sup>1</sup> E & R Raman and Ramanathan's formula corrected for orientation scattering.

<sup>2</sup> J. C. K. Formula given by equation (41).

A graph fig. 1 with the percentage volume of toluene as abscissa and the intensity as ordinate is given. The dotted curve shows the observed values and the other one shows the calculated values, from formula (41).

In the above table X and fig. 1 one sees a fairly good agreement between the calculated and observed values.

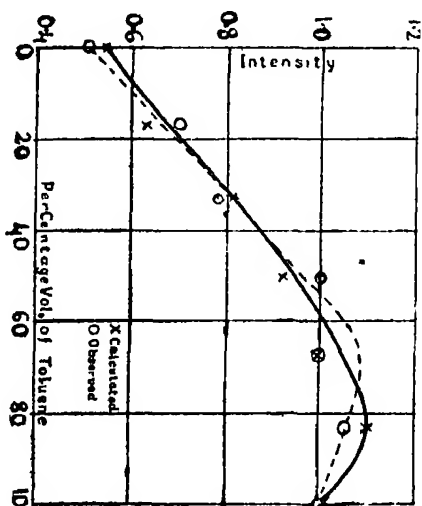


Fig. 1.

We shall now consider the intensity of scattered light by mixtures of methyl alcohol and carbon bisulphide at different temperatures. In the calculations carbon bisulphide is taken as the second component and methyl alcohol as the first. In calculating the density and concentration scattering the common multiplying factor  $1/N\lambda^4$  is omitted as in the previous case. Experimental data for the compressibilities of the mixture are not available. The variation of compressibility with concentration is assumed to be similar to the mixtures of carbon bisulphide and methyl alcohol (for which data is available), the relation being almost linear. The necessary correction for variation with temperature is also made.

The variation of refractive index with concentration is calculated as before for the F line and for calculating

variations with temperature Lorentz's formula is employed. The following table gives the squares of the refractive indices for different concentrations and temperatures.

TABLE XI.  
SQUARES OF REFRACTIVE INDICES

Temp.	CH <sub>3</sub> OH	K=0.12	K=0.25	K=0.43	K=0.67	K=1.0	K=1.5	K=2.33	K=4.0	K=9.0	CS <sub>2</sub>
20	1.777	1.827	1.884	1.943	2.016	2.095	.	.	.	.	2.732
30	1.769	1.814	1.872	1.929	1.995	2.077	.	.	.	2.529	2.699
40	1.754	1.802	1.860	1.914	1.983	2.060	2.155	2.249	2.364	2.502	2.670
50	1.744	1.791	1.858	1.901	1.968	2.041	2.138	2.229	2.344	2.478	2.640
60	1.733	1.778	1.840	1.887	1.952	2.028	2.120	2.208	2.320	2.453	2.611

The compressibilities and the squares of the refractive indices for different concentrations and temperatures being known, and knowing  $R$  to be equal to  $83.15 \times 10^6$  C. G. S. units, the values of  $\Omega_1 \cdot N\lambda^4$  are calculated. The values of  $\partial \epsilon / \partial k$  for different temperatures and concentrations are obtained as in the previous case. There now remains the factor  $\partial \log p_2 / \partial k$  to calculate the concentration scattering. In the absence of experimental data recourse had to be taken to theoretical methods of calculation. The total vapour pressures for different concentrations and temperatures are first determined by the usual method. For temperatures above the critical solution temperature Porter's method<sup>1</sup> was applied by using the formula.

$$P = \Pi_a \mu_a e^{\beta(1-\mu_a)^2} + \Pi_b \mu_b e^{\beta \mu^2} \quad \dots (43)$$

where  $P$  is the total vapour pressure,  $\Pi_a$  and  $\Pi_b$  are the vapour pressures of the two constituents at the same temperature,  $\mu_a$  and  $\mu_b$  are the molecular fractions of the two constituents, and  $\beta$  is a constant slightly decreasing with increasing temperatures. All the quantities in the above equation except  $\beta$  are known. After getting a proper value of  $\beta$ , the partial vapour pressures are calculated from the

<sup>1</sup> Trans. Farad. Soc., Vol. XVI, p. 336.

formula

$$\pi_a = \Pi_a \mu_a e^{\beta(1-\mu_a)^2}$$

where  $\pi_a$  is the partial pressure corresponding to the molar fraction  $\mu_a$ . This approximate but very useful formula, which fitted in well for temperatures above the critical temperature, failed to give concordant results for lower temperatures. For these temperatures, Marshall's graphical method<sup>1</sup> which is also based on the general solution of Duhem's equation was used. This method though very tedious, was found to give more concordant results. The above methods of calculating partial vapour pressures are also justified by the fact, that when they are applied to cases where experimental data are available, the calculated values agreed very well with the experimental values. The results of these calculations for mixtures of methyl alcohol and carbon bisulphide are given in the following fig. 2.

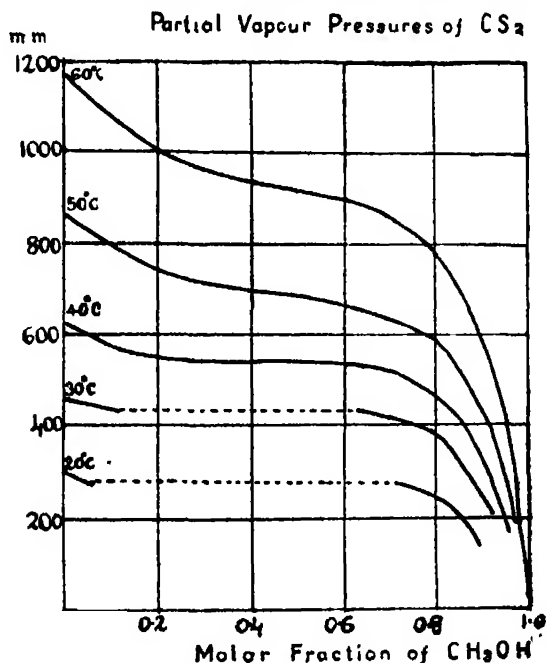


Fig. 2.

The molar fractions of methyl alcohol are given as abscissa and the partial vapour pressure of carbon bisulphide as ordinate. It is easily seen from the curve corresponding to the critical solution temperature, that there is a point of inflection. For curves corresponding to lower temperatures there are two concentrations corresponding to the two layers for which the partial pressure is the same. To get the values of  $\partial \log p_2 / \partial k$ , the above graphs are redrawn with  $k$  as abscissa and  $\log p_2$  as ordinates and from these graphs the values of  $\partial \log p_2 / \partial k$  are calculated. Thus all factors being known,  $\alpha_1$ ,  $N\lambda^4$  is easily calculated.

The orientation scattering for any temperature for methyl alcohol and carbon bisulphide is calculated from (41a) as in the previous case. From these, the values for other concentrations are easily calculated from (35).

The following tables give the calculated and observed intensities for the transversely scattered light, for different temperatures and different concentrations.

TABLE XII (a)

 $t = 20^\circ\text{C}$ 

Liquid	Percentage Volume of $\text{CS}_2$	Concentration $K = m_2/m_1$	$\alpha_1 \cdot N\lambda^4$	$\alpha_2 \cdot N\lambda^4$	$4Q_2 \cdot N\lambda^4$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						J.C.K.	R&R	Calculate 1		Observed
								R&R	J.C.K.	
$\text{CH}_3\text{OH}$	0	.	14	0	1	17	15	0.05	0.08	0.08
A	25	0.5	21	96	65	183	182	0.6	0.60	0.72
B	40	1.0	28	1264	110	1673	1402	5.0	5.1	5.0
$\text{CS}_2$	100	.	77	0	359	714	436	1.5	2.5	1.5

TABLE XII (b).

 $t = 30^{\circ}\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\alpha_1 \cdot N\lambda^*$	$\alpha_2 \cdot N\lambda^*$	$4\alpha_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						R&R	J C K	Calculated		Observed
								R&R	J C K.	
$\text{CH}_3\text{OH}$	0	.	15	0	1.5	16.5	18	0.06	0.06	0.08
A	25	0.5	22	96	69	187	185	0.6	0.6	0.74
B	48	1.4	30	1407	47	1644	1708	5.9	6.0	6.5
$\text{CS}_2$	100	.	82.6	0	386	469	765	1.7	2.6	1.6

TABLE XII (c).

 $t = 40.5^{\circ}\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\alpha_1 \cdot N\lambda^*$	$\alpha_2 \cdot N\lambda^*$	$4\alpha_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						R&R	J C K	Calculated		Observed
								R&R	J C K.	
$\text{CH}_3\text{OH}$	0	.	16	0	2	18	20	0.08	0.07	.1
A	25	0.5	23	157	72	251	242	0.9	0.85	.90
B	50	1.6	38	5350	166	5554	6008	20	21	23
C	75	5.0	16.7	8	270	inf	inf	inf.	inf.	80
$\text{CS}_2$	100	...	87	0	407	494	807	1.75	2.6	1.75

TABLE XII (d).

 $t = 50^{\circ}\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\alpha_1 \cdot N\lambda^*$	$\alpha_2 \cdot N\lambda^*$	$4\alpha_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						R&R	J C K	Calculated		Observed
								R&R	J C K	
$\text{CH}_3\text{OH}$	0	...	17.2	0	2	19	21.5	0.07	0.07	0.1
A	25	0.5	25.2	142	76	243	277	0.9	1.0	1
B	50	1.6	40.6	2246	171	2458	2663	8.4	9.0	14.5
C	75	5.0	65.6	5432	284	5782	6077	20	21	16
$\text{CS}_2$	100	...	91.6	0	427	519	853	1.8	2.9	1.7



TABLE XII (e).

 $t=60^{\circ}\text{C}$ 

Liquid	Percentage Vol of CS <sub>2</sub>	K	n <sub>1</sub> NA*	n <sub>2</sub> NA*	4n <sub>1</sub> NA*	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						Calculated		Calculated		Observed
						R&R	J O K	R&R	J O K.	
CH <sub>3</sub> OH	0		18.4	0	2	20.4	22.1	0.07	0.08	0.1
A	25	0.5	26.7	200	81	308	381.6	1.0	1.31	1.33
B	50	1.0	43	1180	180	1403	1523	5.0	5.3	6
C	75	5.0	69	1706	283	2118	2285	7.3	8.0	9
CS <sub>2</sub>	100		96	0	440	545	890	1.9	3.1	2

Three typical graphs corresponding to tables XIIb, XIIc and XIId are drawn. The percentage volume of carbon bisulphide is given as abscissa and the intensity as ordinate. The dotted lines in all cases denote the observed values.

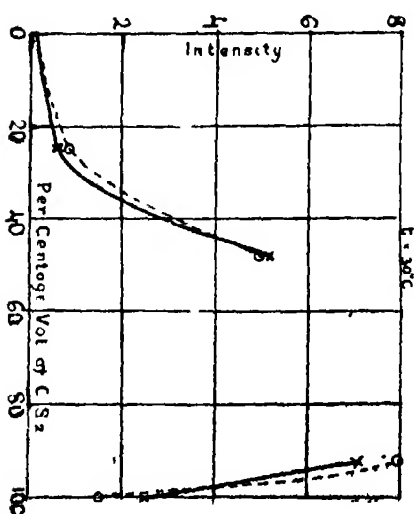


Fig. 3.

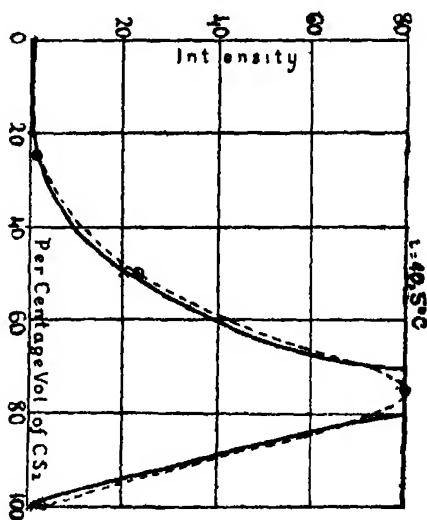


Fig. 4.

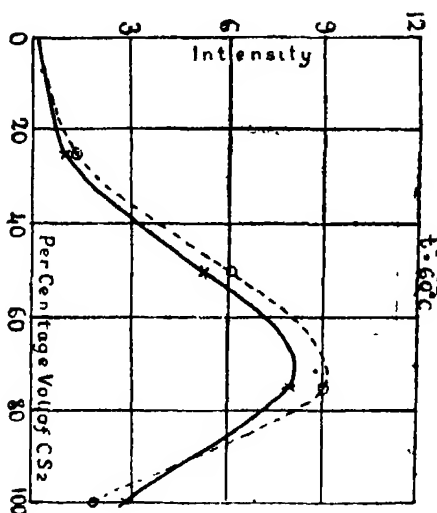


Fig 5.

## 2. POLARISATION.

Knowing the values of  $\gamma$  for Toluene and acetic acid, obtained by direct observation, the values of  $\gamma$  for the mixtures are calculated from (41a) neglecting  $\alpha_s$ . The calculated and observed values are given in the following table for comparison :

TABLE XIII.

Liquid	Percentage Vol of Toluene	K	100 $\gamma$	
			Calculated.	Observed.
Toluene	100		55	55
A	83.3	24	51	46.5
B	66.7	.61	39	37.8
C	50	1.21	35	33.8
D	33.3	2.43	35	32.5
E	16.7	6.07	44	45.6
Acetic Acid	0		58.5	58.5

A graph Fig. 6 with percentage volume of toluene as abscissa and  $100\gamma$  as ordinate is also given.

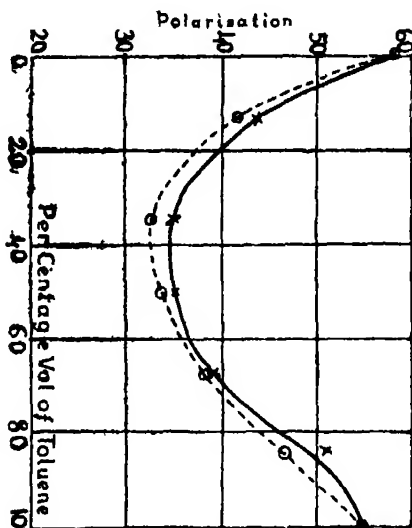


Fig. 6.

In a similar way, knowing the values of  $\gamma$  for methyl alcohol and carbon bisulphide obtained by direct observation, the values of  $100\gamma$  for the mixtures are calculated as before. The calculated and observed values for different temperatures and concentrations are given in the following tables.

TABLE XIV (a).

$t = 20^\circ\text{C}$

Liquid.	Percentage Vol. of $\text{CS}_2$	K	$100\gamma$	
			Calculated	Observed.
$\text{CH}_3\text{OH}$	0	..	9	9
A	25	0.5	22	30.3
B	40	1.0	4.1	9
$\text{CS}_2$	100	...	70	70

TABLE XIV (b).

 $t = 30^{\circ}\text{C}$ 

Liquid	Percent Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated	Observed
$\text{CH}_3\text{OH}$	0		9	9
A	25	0.5	22	20
B	48	1.4	4.7	6
$\text{CS}_2$	100	.	70	70

TABLE XIV (c).

 $t = 40.5^{\circ}\text{C}$ 

Liquid	Percent Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated	Observed
$\text{CH}_3\text{OH}$	0		9	9
A	25	0.5	16.7	16.3
B	50	1.6	1.5	5.1
C	75	5.0	0	3.0
$\text{CS}_2$	100		70	70

TABLE XIV (d).

 $t = 56^{\circ}\text{C}$ 

Liquid	Percent Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated	Observed
$\text{CH}_3\text{OH}$	0		9	9
A	25	0.5	18.5	22.5
B	50	1.6	3.6	7
C	75	5.0	2.5	4.6
$\text{CS}_2$	100	.	69	96

TABLE XIV(e).

 $t = 60^\circ\text{C}$ 

Liquid	Percent Vol of $\text{CS}_2$	K	100 $\gamma$	
			Calculated	Observed
$\text{CH}_3\text{OH}$	0		9	9
A	25	0.5	15	23
B	50	1.6	7	10
C	75	0.5	7	10
$\text{CS}_2$	100		69	69

Two typical graphs corresponding to Tables XIVc and XIVe are given in figures (7) and (8). The percentage volumes of  $\text{CS}_2$  are given as abscissa and 100 $\gamma$  as the ordinate. The tables and figures show also a fair agreement between theory and experiment.

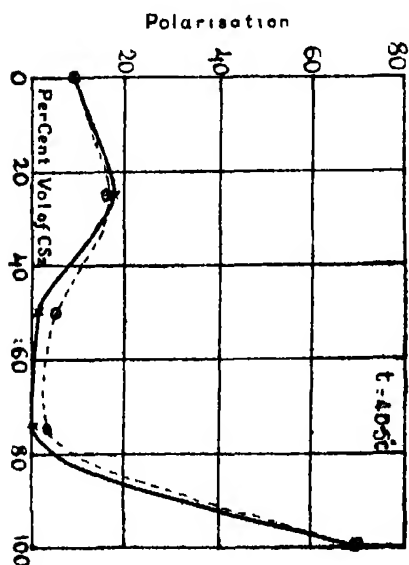


Fig. 7.

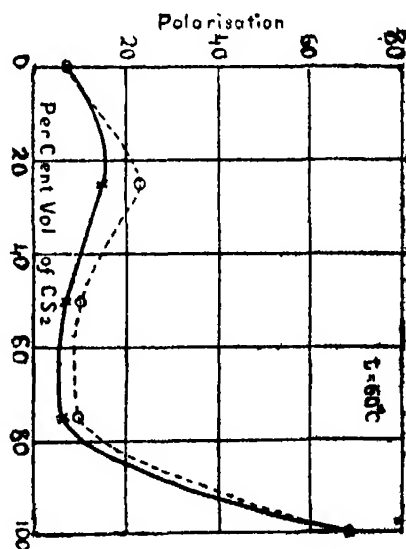


Fig. 8.

## PART IV.

*Summary and Conclusion.*

The paper describes experimental and theoretical work dealing with the scattering of light by binary liquid mixtures. Part I deals with the experimental work done on measurement of the intensity of light scattered by mixtures of toluene and acetic acid at the room temperature and by mixtures of methyl alcohol and carbon bisulphide at different temperatures. It gives also the state of polarisation of the scattered light for the same pairs of liquids. The variation of the intensity of light scattered by the second pair of liquids is very interesting and instructive. The intensity at any temperature increases with concentration till a particular concentration is reached beyond which it again decreases. This effect is very great at the critical temperature while for the critical concentration, the intensity is enormous, but above and below this, it decreases. The state of polarisation shows also similar interesting changes. For any temperature, the imperfectness of polarisation is a minimum for a particular concentration; this effect being more prominent at the critical temperature: at which the scattered light is almost completely polarised for the critical concentration, the light becomes more and more imperfectly polarised at higher or lower temperatures.

Part II, art. 2, discusses an electromagnetic theory of the scattering of light in binary liquid mixtures without assuming a molecular structure, on the basis of Lorentz's treatment of the scattering of light in gases. By this method Raman and Ramanathan's formula is derived. The same result is shown to follow if the medium is endowed with a molecular structure and the molecules are assumed to be isotropic. The same treatment is extended to the case of anisotropic molecules,

in which case it is shown that if the molecules are entirely oriented at random, the transversely scattered light is imperfectly polarised. The intensity of the light scattered in a direction at right angles to the primary beam is shown to be

$$\frac{V}{r^2} \left[ \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (\epsilon-1)^2 (\epsilon+2)^2 + \frac{M_2 (\partial \epsilon / \partial k)^2}{N\lambda^4 \cdot m_1 \partial \log p_1 / \partial k} \right] \frac{6(1+r)}{6-7r}$$

Part III gives the comparison of the results obtained by theory and experiment and shows a fair agreement between the two.

In conclusion, the author wishes to express his best thanks to Prof. C. V. Raman who suggested the problem, for his helpful interest and encouragement.

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# On the Modification of the Laws of Emission of Ions from Hot Metals by the Quantum Theory <sup>1</sup>

By

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1. *Introduction.*—Although the classical electron theories of metals, developed by Drude, Lorentz, Thomson and others, have given us a fair account of the various outstanding physical properties of metals,—such as the heat and electrical conductivity, the Peltier-effect, the Thomson-effect, the Richardson-effect and so on, the various secondary hypotheses which have been advanced to explain these phenomena are seldom convincing and are often in absolute contradiction with one another. The most obvious difficulty, however, is the question of the heat-capacity of metals. If the ‘free’ conduction electrons could claim their full share in the equal distribution of kinetic energy, then this share of energy should be plainly noticeable in the atomic heats of these bodies. Such an increase in the atomic heats of metals as compared to metalloids which contain vanishingly few free electrons, has never been discovered. Further, as Lorentz has pointed out, the classical electron theory invariably leads to Raleigh’s law of radiation.

In recent years, the ideas have been developing that the law of equipartition of energy for the metallic electrons, has got to be abandoned in favour of Planck’s quantum law. The difficulty, however, lies in properly quantizing the motions of the metallic electrons and in explaining the thermal

<sup>1</sup> Read before Bangalore session of Indian Science Congress, 1923



conductivity of metals and the correctness of Wiedemann-Franz's law on such a quantized theory. Prof. Lindemann<sup>1</sup> has pointed out that the expression 'free' electron suggesting or intending to suggest an electron normally not under the action of any force, is really a contradiction in terms. If the electrons be not attracted by atomic residues (and this assumption is essential to prevent re-combination) the repulsion between the electrons themselves will prevent their being free in the true sense. It is, therefore, conceivable that metallic electrons instead of forming an ideal gas, really constitute a condensed solid. In continuation of the conceptions of Born and Kármán, one may suppose that a metal crystal is constituted of inter-locked space lattices of electrons, atoms or atomic residues. Prof. Lindemann<sup>2</sup> has, already, chalked out a theory of metallic state on the basis of these ideas. Prof. J. J. Thomson<sup>3</sup> has, recently, developed such and similar ideas in his electron theory of solids.

The object of the present paper is to consider statistically the laws of emission of ions or electrons from hot metals on the basis of the supposition that the metallic ions or electrons behave in all manner like Planck's line vibrators while the emitted ones constitute an ideal monatomic gas.

2. *Temperature Equilibrium between the emitted Ions or Electrons with emitting Metal Crystal.*—The problem before us is to determine statistically the temperature equilibrium of a hot metal-crystal with the radiant energy of æther and with an atmosphere of gaseous ions or electrons contained in a vacuous enclosure of volume  $V$  and maintained at a temperature  $T^\circ A$ . The assembly for our present statistical calculations embraces various types of systems—æther, free gaseous ions or electrons, and condensed electrons,

<sup>1</sup> 'Phil. Mag.,' Vol. 29, 1915, p. 127

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Phil. Mag., Vol 48, p. 721, 1922

atoms or atomic residues in the solid state. One<sup>1</sup> can formally include all the various systems into the statistical calculations. It will, however, conduce to brevity and clearness if one assumes that the sublimation of ions or electrons takes place quite independently and does not alter the average distribution of energy amongst other systems of the assembly. The distribution of energy in any type of systems in an assembly depends on the motion of that system alone so long as it is not too frequently interfered with,—such an assumption of limited interference being fundamental to all statistical calculations.

Let us limit our considerations to any example of an assembly of  $M$  ions or electrons of which  $1, 2 \dots N$  are in the vapour phase while  $N + 1, \dots M$  are in the solid phase; so that the number in the solid phase is  $S = M - N$ . We will suppose that the particles in the vapour-phase form an ideal monatomic gas while those in the condensed state constitute Planck's resonators capable of taking energies in multiples of quanta  $\epsilon_i = h\nu_i$  ( $i = 1, 2, 3$ , etc.). The mechanism by which the resonators pass from the condensed phase to the free gaseous state, is not known. It may be either radiative or due to collision. Statistically we may suppose that  $\phi$  is the work done at the absolute zero of temperature in taking out a particle from the solid to the vapour phase. Now if  $q$ 's and  $p$ 's specify the positional and momenta co-ordinates of the gaseous particles, their energy content with respect to a standard zero state of energy, may be written as,

$$E_g = \frac{1}{2m} \sum_{i=1}^{i=3N} p_i^2 + N\phi \quad \dots (1)$$

The energy of the resonators in the condensed solid phase may

<sup>1</sup> Messrs. Darwin and Fowler's new statistical method lends itself to be utilised for a more elegant treatment of the present subject. (Phil. Mag., Vol. 44, September and November, 1922; Vol. 45, January and March, 1923, and other subsequent papers).

be written in the form,

$$E_f = \sum_{i=1}^{i=3S} \epsilon_i = \frac{1}{2m} \sum_{i=1}^{i=3S} (p_i'^2 + 4\pi^2 m^2 \nu_i^2 q_i'^2) \quad \dots (2)$$

where,  $\nu$ 's specify the natural frequencies of the resonators. The probability that the particles 1, 2 ... N are in the vapour phase while N + 1, ... M are in the solid phase, is according to Boltzmann's theorem,

$$\omega = A f e^{-\frac{(E_g + E_f)}{kT}} (dp_1 dq_1 \dots dp_{3N} dq_{3N}) (dp'_1 dq'_1 \dots dp'_{3S} dq'_{3S}) \dots (3)$$

Now, since the gaseous particles are governed by the classical laws of mechanics, we have,

$$\begin{aligned} \int e^{-\frac{E_g}{kT}} dp_1 \dots dp_{3N} \cdot dq_1 \dots dq_{3N} \\ = e^{-\frac{N\phi}{kT}} (2\pi m kT)^{\frac{3N}{2}} V^N \end{aligned} \quad \dots (4)$$

where, the integration has been carried throughout the volume V (neglecting the volume of the metal crystal) from  $p = \alpha$  to  $p = -\alpha$ .

In order to evaluate the integral

$$\int e^{-\frac{E_f}{kT}} dp'_1 dq'_1 \dots dp'_{3S} dq'_{3S}$$

in the light of the quantum statistics, let us introduce the auxiliary variables  $\xi_i$  and  $\eta_i$  defined by,

$$\left. \begin{aligned} \xi_i &= \pi \nu_i q_i \sqrt{2m} \\ \eta_i &= \frac{p'_i}{\sqrt{2m}} \end{aligned} \right\} \quad \dots (5)$$

So that we obtain

$$\epsilon_i = \xi_i^2 + \eta_i^2 \quad \dots (6)$$

and hence

$$\left. \begin{aligned} \xi_i &= \sqrt{\epsilon_i} \cos \phi_i \\ \eta_i &= \sqrt{\epsilon_i} \sin \phi_i \end{aligned} \right\} \quad \dots (7)$$

where,  $\phi_i$  is a parametric angle. we have thus,

$$dp', dq'_i = \frac{1}{\pi v_i} d\xi_i d\eta_i = \frac{1}{2\pi v_i} d\epsilon_i d\phi_i \quad \dots (8)$$

$$\therefore \int \int e^{-\frac{\epsilon_i}{kT}} dp', dq'_i = \int \int_{\phi_i=0}^{2\pi} e^{-\frac{\epsilon_i}{kT}} d\epsilon_i \frac{d\phi_i}{2\pi v_i} = \int e^{-\frac{\epsilon_i}{kT}} \frac{d\epsilon_i}{v_i} \quad \dots (9)$$

Planck's quantum statistics of the oscillators require that  $\epsilon_i$  can assume only discrete values, so that  $d\epsilon_i = h\nu_i$ . Hence the integral (9) changes to the sum,

$$\sum_{n=0}^{\infty} e^{-\frac{nh\nu_i}{kT}} \frac{h\nu_i}{v_i} = \frac{h}{1 - e^{-\frac{h\nu_i}{kT}}} \quad \dots (10)$$

Hence the probability takes the form,

$$\omega = A \cdot e^{-\frac{N\phi}{kT}} (2\pi mkT)^{\frac{3N}{2}} V^N \frac{h^{3S}}{\prod_{i=1}^{3S} \left(1 - e^{-\frac{h\nu_i}{kT}}\right)} \quad \dots (11)$$

where,  $\Pi_{3S}$  denotes the product of such functions as

$$\left(1 - e^{-\frac{h\nu_i}{kT}}\right) [i=1, 2, 3S].$$

Let us now consider the two special cases of relation (11).

*Case 1.* In the case of resonators for which  $h\nu$ , is large compared to  $kT$ , we have the probability,

$$\omega = e^{-\frac{N\phi_0}{kT}} \frac{3N}{(2\pi mkT)^{\frac{3}{2}}} \frac{1}{V^N} \frac{1}{h^{3S}} \quad \dots (12)$$

*Case 2.* On the other hand if the frequencies of the resonators be so low that  $h\nu$ , is small compared to  $kT$ , we have

$$\omega = e^{-\frac{N\phi_0}{kT}} \frac{3N}{(2\pi mkT)^{\frac{3}{2}}} \frac{1}{V^N} \left( \frac{kT}{r} \right)^{3S} \quad \dots (13)$$

where,  $\bar{\nu}$  is the geometric mean of the spectrum of frequencies.

Now the total number of  $M$  particles can be made into groups of  $N$  and  $S$  in  $\frac{M!}{N!S!}$  ways while the  $S$  particles inside the metal-crystal can be arranged in lattices in  $S!$  ways. Hence the total probability becomes,

$$W = \frac{M!}{N!S!} S! \omega \quad \dots (14)$$

The equilibrium state of an assembly corresponds to the state of maximum probability for which we must have

$$\frac{\partial W}{\partial N} = 0 \quad \text{or} \quad \frac{\partial}{\partial N} \log W = 0.$$

Hence using Stirling's approximation in the form  $N! = N \log N - N$ , we obtain in the first case

$$\log \frac{N}{V} = -\frac{\phi_0}{kT} + \log \left( \frac{2\pi mkT}{h^3} \right)^{3/2} \frac{1}{V^3} \quad \dots (15)$$

and in the second case

$$\log \frac{N}{V} = -\frac{\phi_0}{kT} + \log \left( \frac{2\pi mkT}{kT} \right)^{3/2} \frac{1}{V^3} \quad \dots (16)$$

3. *Law of emission of Electrons.*—The electron space-lattices may possess a large number of proper frequencies and as Prof. Lindemann has pointed out, Planck's infinite number of resonators may have a physical meaning. One would, however, require special assumptions to calculate the proper frequencies of the electron space lattices. The experimental fact, namely that the electrical resistance of metals is altered only by alternating currents of very high frequencies of the order of  $10^{14}$  periods per second (as when infra-red light is reflected from metals), points to the fact that the metallic electrons must possess very high frequencies. One however does not know the lowest limit of the electronic frequencies. One may tentatively suppose that the observed frequency of the photoelectric threshold sets a limit to the lowest frequency of the metallic electrons. Ultraviolet light impinging on an electronic lattice, lets loose the electrons and projects them out. This can readily happen only when the natural frequencies of the electronic space-lattices are in resonance with the impinging light wave. In any case it is quite conceivable that metallic electrons, owing to their small mass, possess extremely high frequencies the lowest limit of which ranges from  $10^{14}$  to  $10^{15}$  for different metals. If this be so, then for the metallic electrons  $\frac{h\nu_e}{kT}$  will be much larger than unity at all temperatures available in the laboratory. Hence we can write for the equilibrium-concentration  $n_-$  of electrons near a hot metal crystal at temperature  $T^\circ A$ ,

$$n_- = \frac{(2\pi m_- kT)}{h^3} e^{\frac{3}{2} - \frac{\phi_0}{kT}} \quad \dots (17)$$

As Prof. Richardson<sup>1</sup> has pointed out, in thermionic current measurements, we do not really measure the equilibrium concentration of electrons, but the number emitted per second

<sup>1</sup> "The Emission of Electricity from Hot Bodies,"—2nd Ed., 1921, pp. 314 and 55.

per unit area of the hot body. This number  $n'_-$  is equal to  $(1-r)$  times the number reaching the body per second, where  $r$  is the fraction of the incident electrons sent back by reflection. According to the kinetic theory of gases,

$$n'_- = (1-r) n \left( \frac{kT}{2\pi m_-} \right)^{\frac{1}{2}} = (1-r) \frac{2\pi k^3 m_-}{h^3} \cdot T^{\frac{3}{2}} \cdot e^{-\frac{\phi_-}{kT}} \quad (18)$$

Hence the thermionic emission of electrons per second per unit area, is given by the expression,<sup>1</sup>

$$I_- = n'_- \delta = (1-r) \frac{2\pi k^3 \delta m_-}{h^3} T^{\frac{3}{2}} \cdot e^{-\frac{\phi_-}{kT}} \quad \dots (19)$$

where,  $\delta$  = electronic charge.

4. *Thermionic Emission of positive ions.*—The positive ions, owing to their larger mass, would possess much lower frequencies and for temperatures within the range  $1000^\circ\text{A}$  to  $2000^\circ\text{A}$ , one may reasonably suppose that  $h\nu_i$  is small compared to  $kT$ , and so we have for the equilibrium-concentration of positive ions,

$$n_+ = \left( \frac{2\pi m_+}{kT} \right)^{\frac{3}{2}} \frac{1}{\nu_+} e^{-\frac{\phi_+}{kT}} \quad \dots (20)$$

The thermionic emission of positive ions per second per unit area is

$$I_+ = \left( \frac{2\pi m_+}{k} \right)^{\frac{3}{2}} \delta \frac{\bar{\nu}_+}{T^{\frac{3}{2}}} e^{-\frac{\phi_+}{kT}} \quad \dots (21)$$

In the absence of any further knowledge of  $\bar{\nu}_+$ , we cannot put expression (21) to an experimental test. But the relation (19) contains no unknown constants except the work-function

<sup>1</sup> Laue has worked out the same expression by thermodynamical arguments (Jahrb. d. Radioaktivität 15, 205 U 257, 1918; and Ann der Phys. Vol. 58, 1919, p. 696). Dushman, Phys. Rev., June, 1923.

$\phi_-$  a knowledge of which should enable us to predict theoretically the rate of emission of electrons from different metals at various temperatures under perfect vacuum conditions.

5. *The Nature of the work-function  $\phi_-$ .*—The fact that the emission of electrons is attended by a cooling effect while absorption results in a heating effect, suggests that the emission may be regarded as a process of sublimation of electrons from the solid to the gaseous phase and we can designate  $\phi_-$  in heat units as the 'heat of sublimation' or 'heat of condensation' of electrons at the absolute zero of temperature. On the other hand this work-function in equivalent volts should be analogous to the ionisation potential of gases and vapours. The recent work of Compton and others on low voltage arcs in gases and vapours, has brought to light the interesting fact that the ionisation potentials of vapours are not constant but may be much less for atoms brought to an abnormal condition by absorption of radiation generated in other atoms. The ionisation potential therefore may be shifted back to the first resonance potential as its limiting value. The closeness of atoms in the condensed state will certainly loosen the electrons on the surface of the atoms. We should, therefore expect the ionisation potentials of elements in the condensed state to be much diminished. It is unfortunate that we know very little as yet about the exact nature of 'loosening' of the electrons inside a metal, or about the mechanism of emission, which may be either radiative or due to collision. It is however quite probable that both radiation and collision are simultaneously operative in the actual processes involved. But it would introduce much simplification into the theory if one single mechanism could explain the emission. The argument against the view that the thermionic emission may be regarded as due to the radiation of the hot body itself is that the magnitude of the auto-photo-electric currents is much lower than the thermionic currents. This is, however, to be expected. For by impinging



radiation from outside on metals, we do not really attain to the condition of radiation due to the hot body itself. If thermionic emission of electrons were due to the radiation of the hot body itself, then the type of arguments advanced by Prof. Richardson<sup>1</sup> in his statistical theory of photo-electric effect, should apply to the case of thermionic emission. According to his statistical theory the average kinetic energy of electrons emitted by radiation of frequency  $\nu$  is given by,

$$\bar{T} = h\nu - \phi \quad \dots (22)$$

Hence for electrons emitted with zero kinetic energy, we should have,

$$0 = h\nu_0 - \phi_0 \quad \dots (23)$$

where,  $\nu_0$  is the frequency of the photo-electric threshold. There is no *a priori* reason why  $\phi_0$  and  $\phi_-$  should not be identical. But the experimental observations on both thermionic and photo-electric effects are so hopelessly conflicting and uncertain that no one can as yet pronounce any decision on this point with any degree of certainty. It appears to me that if some theoretical expression could be found for the calculation of the long-wave-length limit, it might serve some useful end in this connection. One such way is indicated below. Prof. Richardson's<sup>2</sup> statistical theory of photo-electric effect leads to the relation,

$$\nu_0 = \frac{1}{3}\nu_m \quad \dots (24)$$

where  $\nu_m$  is the frequency of the maximum selective photo-electric effect. Prof. J. J. Thomson<sup>3</sup> in his recent developments of the electron theory of metals, has given us a method of calculating the frequency of the selective photo-electric

<sup>1</sup> Phil. Mag., Vol. 23, p. 594, 1912; Vol. 25, p. 574, 1912.

<sup>2</sup> Loc. cit.

<sup>3</sup> Loc. cit.

effect. In the case of monovalent alkali metals,

$$\nu_{\infty} = \frac{(5.224)^{\frac{1}{2}}}{2\pi m^{\frac{1}{2}}} \delta \left( \frac{A}{M} \right)^{\frac{1}{2}} = 4.526 \times 10^{10} V^{\frac{1}{2}} \quad \dots (25)$$

where  $V$  is the atomic volume of the elements. Combining (24) and (25), we obtain an expression for the long-wave-length limit of alkali metals in the form,

$$\lambda_0 = .9942 \times 10^{10} V^{\frac{1}{2}} \text{ cms} \quad \dots (26)$$

This expression appears to apply quite satisfactorily to a large number of metals irrespective of any question of valency. But to assume that the electronic structure of all these metals is the same as that of alkali metals is certainly far from convincing. One should, however, find no difficulty in working out similar expressions for polyvalent metals with different arrangements of electrons on the lines indicated by Prof. J. J. Thomson. The multiplying factor of  $V^{\frac{1}{2}}$  in the expression (26) on numerical computation, however, yields nearly the same value with various different arrangements of electrons except for the divalent elements. Apart from the question of valency and structure, the validity of such calculations of  $\lambda_0$  rests on the assumption of the existence of selective photo-electric effect in all metals. One does not know whether the selective effect is due to peculiarly numerous proper frequencies within a small region or due to other intra-atomic electrons. In any case, there is, *a priori*, no reason why all metals should not show selective photo-electric effect.

In the following pages are given certain calculations based on the photo-electric and thermionic data of various reliable observers to test the identity of photo-electric and thermionic work-functions.

6. *Method of calculations.*—For most metals  $r$  has the value  $^1 \cdot 5$  nearly. And since the exponential factor in the expression for emission is relatively more important, the percentage of error introduced in the value of  $I_-$  will be inappreciable on putting  $r$  equal to  $\cdot 5$  even in cases of metals in which its value differs from this by a small amount. Hence taking  $r = \cdot 5$  generally in the expression (19), we have,

$$I_- = \frac{\pi m_e k^2}{h^3} T^2 e^{-\frac{\phi_-}{kT}} = A T^2 e^{-\frac{b}{T}} \quad \dots (27)$$

using the values,

$$k = 1.372 \times 10^{-10} \text{ ergs/deg}$$

$$h = 6.55 \times 10^{-27} \text{ erg/sec.}$$

$$m = 8.995 \times 10^{-28} \text{ grams.}$$

$$e = 4.774 \times 10^{-10} \text{ E S U}$$

we have,

$$A = 9 \times 10^{10} \text{ E S U/cm}^2 \text{ deg}^2.$$

$$= 30.1 \text{ amp/cm}^2 \text{ deg}^2$$

$$\therefore I_- = 30.1 T^2 e^{-\frac{b}{T}} \quad \dots (27)$$

$$\log_{10} I_- = 1.4786 + 2 \log_{10} T - \frac{b}{2.303T} \quad \dots (28)$$

Thermionic work-function,

$$\phi_{\text{therm}} = \frac{kb}{e} = .862 \times 10^{-8} b \text{ volts} \quad \dots (29)$$

Photo-electric work-function,

$$\phi_{\text{phot}} = \frac{h\nu_0}{e} = \frac{12.36}{\lambda_0} \times 10^{-8} \text{ volts} \quad \dots (30)$$

<sup>1</sup> A. Gehrts (Ann. d. Phys. 36, 985, 1911).

where  $\lambda_0$  is the long wave-length limit of the metals in centimeters.

7. *Comparison of theoretical and experimental values.*

HEAVY METALS.

1. *Platinum.*—The experimental determination of the long wave-length limit of platinum has been made by different investigators. Otto Koppius<sup>1</sup> gives the value  $257\mu\mu$  for  $\lambda_0$ . Messrs.<sup>2</sup> Kober, Sende and Simon have found the value to lie somewhere between  $260\mu\mu$  to  $300\mu\mu$  some of their determinations being at  $283\mu\mu$  and  $285\mu\mu$ . Richardson<sup>3</sup> and Compton's determination from the maximum energy of the photo-electron fixes the value at  $280\mu\mu$ , while that from the mean energy leads to the value  $291\mu\mu$  for  $\lambda_0$ . The two observers, however, consider that their determinations from the mean energies are more accurate. Taking all these facts together one can reasonably suppose that  $291\mu\mu$  is the most probable value for the long wave-length limit for platinum. According to Richardson-Thomson rule,

$$\begin{aligned}\lambda_0 &= .9942 \times 10^{-8} V^{\frac{1}{2}} \text{ cms} \\ &= 296\mu\mu.\end{aligned}$$

Below are given R. Suhrmann's<sup>4</sup> and W. Schlichter's<sup>5</sup> data on emission from platinum under the best vacuum conditions.

R. Suhrmann's data on emission from platinum.

Length of the Pt-foil = 21 mm.

Breadth of the foil = 2 mm.

$$I = \frac{2}{\text{area}} \frac{31 \times 10^{-7}}{n} = 5.5 \times 10^{-7} \text{ n amp}$$

$$b_0 = 2.303 T (1.4786 + 2 \log_{10} T - \log_{10} I)$$

<sup>1</sup> Phys. Rev., Vol. XVIII, No. 6, 1921.

<sup>2</sup> Dissertation Dresden, 1917 (Auszug Phys. Zeitsche), 8562-563, 16, 595, 1915

<sup>3</sup> Phil. Mag., XXIV, p. 576, 1912.

<sup>4</sup> Zeits f. Physik, 13, 1 and 2, pp. 17-34, 1923.

<sup>5</sup> Ann. der Phys., Vol. XLVII, p. 573, 1915.

TABLE I.

$T^{\circ}\text{A}$	$n$	$I$	$\log_{10} I$	$\log_{10} I$	$b_0$
1750	5.8	$3.19 \times 10^{-6}$	3.1959	$-6 + .5038$	48330
1604	11.8	$6.49 \times 10^{-6}$	3.2051	$-6 + .8122$	48300
1639	22.2	$1.221 \times 10^{-5}$	3.2146	$-5 + .0867$	48300
1672	42.2	$2.321 \times 10^{-5}$	3.2232	$-5 + .3057$	48360
1689	58.0	$3.190 \times 10^{-5}$	3.2277	$-5 + .5038$	48350
1722	96.6	$5.313 \times 10^{-5}$	3.2360	$-5 + .7253$	48500
1739	121.6	$6.088 \times 10^{-5}$	3.2402	$-5 + .8253$	48580

mean  $b_0 = 48480$

$\phi_{\text{therm}} = 4.18 \text{ volts.}$

$\therefore \lambda_0 = 295.7 \mu\mu$

W. Schlichter's data on Emission from platinum.

Area =  $23 \text{ cm}^2$ .

TABLE II.

$T^{\circ}\text{A}$	$J$	$I$	$\log_{10} I$	$\log_{10} I$	$b_0$
1195	$1.5 \times 10^{-9}$	$6.5 \times 10^{-11}$	3.0774	$-11 + .8129$	49060
1227	$7.8 \times 10^{-9}$	$3.4 \times 10^{-10}$	3.0888	$-10 + .5315$	48370
1243	$1.35 \times 10^{-8}$	$5.9 \times 10^{-10}$	3.0944	$-10 + .7709$	48480
1291	$6.30 \times 10^{-8}$	$2.74 \times 10^{-9}$	3.1109	$-9 + .4378$	48340
1355	$4.70 \times 10^{-7}$	$2.04 \times 10^{-8}$	3.1319	$-8 + .8096$	48180
1403	$1.08 \times 10^{-6}$	$7.30 \times 10^{-8}$	3.1470	$-8 + .8633$	48190
1451	$5.50 \times 10^{-6}$	$2.39 \times 10^{-7}$	3.1617	$-7 + .3784$	48220
1499	$1.43 \times 10^{-5}$	$6.22 \times 10^{-7}$	3.1759	$-7 + .7938$	48450

mean  $b_0 = 48410$

$\phi_{\text{therm}} = 4.173 \text{ volts.}$

$\therefore \lambda_0 = 296.2 \mu\mu.$

2. *Tungsten*.—Davission<sup>1</sup> and Germer's emission data for Tungsten filament. Area = 0.1825 cm<sup>2</sup>.

TABLE III.

<sup>2</sup> T°A	J	I	log <sub>10</sub> T	log <sub>10</sub> I	b <sub>0</sub>
1923	9 341 × 10 <sup>-5</sup>	5.12 × 10 <sup>-4</sup>	3 2840	-4 + .7091	50200
1973	1 973 × 10 <sup>-4</sup>	1 01 × 10 <sup>-3</sup>	3 2952	-3 + 0340	50160
2021	3 967 × 10 <sup>-4</sup>	2.12 × 10 <sup>-3</sup>	3 3056	-3 + 3373	50050
2069	7.656 × 10 <sup>-4</sup>	4.20 × 10 <sup>-3</sup>	3 3158	-3 + 6228	49960
2113	1 362 × 10 <sup>-3</sup>	7 46 × 10 <sup>-3</sup>	3 3240	-3 + 8729	49780
2162	2 588 × 10 <sup>-3</sup>	1 39 × 10 <sup>-2</sup>	3 3349	-2 + 1443	49790
2207	4 450 × 10 <sup>-3</sup>	2 42 × 10 <sup>-2</sup>	3 3438	-2 + 3828	49720
2247	6 875 × 10 <sup>-3</sup>	3 77 × 10 <sup>-2</sup>	3 3516	-2 + 5761	49720
2298	9 792 × 10 <sup>-3</sup>	5 37 × 10 <sup>-2</sup>	3 3613	-2 + 7297	50100

$$\text{mean } b_0 = 49942$$

$$\phi_{\text{therm}} = 4.30 \text{ volts}^4$$

$$\therefore \lambda_0 = 287.5 \mu\mu$$

Calculated from Langmuir's<sup>3</sup> data,  $b_0 = 44200$ , and  $\phi_{\text{therm}} = 4.23$  volts and hence  $\lambda_0 = 292.2 \mu\mu$ . The atomic volume of Tungsten is a little greater than that of platinum. Hence  $\lambda_0$  for Tungsten should be greater than that for platinum. The only direct observation of the long wave-length-limit of Tungsten is due to M. J. Kelley and Hagenow<sup>4</sup> and the indication of their experiment is that the wave-length of the photo-electric threshold is near about  $230 \mu\mu$ . This result probably gives us only a preliminary idea of the magnitude of the long wave-length limit for Tungsten. Mr. K. K. Smith's<sup>5</sup> thermionic current measurements are, however, in good agreement with Richardson-Thomson rule.

<sup>1</sup> Phys. Rev., Vol. XX, 1922.

<sup>2</sup> Langmuir's temperature scale has been accepted.

<sup>3</sup> Phys. Zeit. Jahrg. 15, p. 525, 1914.

<sup>4</sup> Phys. Rev., Vol. XIII, No. 6, p. 15, 1919.

<sup>5</sup> Phil. Mag., Vol. XXIX, p. 811, 1915.

## Mr. K. K. Smith's emission data on Tungsten—

TABLE IV.

T°A	I	$\log_{10} T$	$\log_{10} I$	$b_0$
1100	$2.56 \times 10^{-12}$	3.0414	-12 + 4282	48400
1200	$1.60 \times 10^{-10}$	3.792	-10 + 2279	49140
1300	$5.83 \times 10^{-9}$	3.1139	-9 + 7657	47720
1400	$1.22 \times 10^{-7}$	3.1461	-7 + 0864	47350
1500	$1.70 \times 10^{-6}$	3.1761	-6 + 2304	47000
1600	$1.71 \times 10^{-5}$	3.2041	-5 + 2330	46630
1700	$1.32 \times 10^{-4}$	3.2304	-4 + 9079	46500
1800	$1.88 \times 10^{-3}$	3.2788	-3 + 2742	47100
2100	$6.70 \times 10^{-2}$	3.3011	-2 + 8260	45180
2300	$6.74 \times 10^{-1}$	3.3619	-1 + 5265	46010

mean  $b_0 = 47010$ . $\phi_{\text{therm}} = 4.05$  volts. $\lambda_0 = 300.2 \mu\mu$ .

According to Thomson-Richardson law,

$$\lambda_0 = .9942 \times 10^{-7} \times \left( \frac{183}{19.2} \right)^{\frac{1}{2}} \text{ cms}$$

$$= 306.2 \mu\mu.$$

$$\therefore \phi_{\text{phot}} = 4.03 \text{ volts.}$$

3. *Tantalum*.—The long wave-length-limit of Tantalum has not been directly observed. But according to Thomson-Richardson law

$$\lambda_0 = .9942 \times 10^{-7} \left( \frac{181.5}{16.6} \right)^{\frac{1}{2}} = 328.3 \mu\mu$$

$$\phi_{\text{phot}} = 3.77 \text{ volts.}$$

Computed from Langmuir's<sup>1</sup> thermionic data of Tantalum,  $\phi_{\text{therm}} = 4.03$  volts, which corresponds to  $\lambda_0 = 307 \mu\mu$  nearly.

<sup>1</sup> Phys. Rev., Vol. II, p. 450, 1918.

Suhrmann's<sup>1</sup> very recent emission data of Tantalum are however, in very good agreement with Thomson-Richardson rule.

$$I = 5.5 \times 10^{-7} n \text{ amps.}$$

TABLE V.

$T^{\circ}\text{A}$	$n$	$I$	$\log_{10} T$	$\log_{10} I$	$b_0$
1440	8.0	..	3.1584	-6 + 6435	43610
1497	22.0	.	3.1753	-5 + 0828	43950
1549	59.2		3.1900	-5 + 5127	44020
1600	130.0		3.2041	-5 + 8543	44220
1628	190.0	.	3.2116	-4 + 0192	44520
1651	273.0	..	3.2178	-4 + 1766	446.0
1679	370.0	..	3.2251	-4 + 3016	44870

$$\text{mean } b_0 = 44400.$$

$$\phi_{\text{therm}} = 3.82 \text{ volts.}$$

$$\therefore \lambda_0 = 323.4 \mu\mu.$$

Langmuir's and other observer's emission data on Molybdenum, Thorium, etc., have been tested in the same manner. They are not elaborately dealt with here, so as not to extend this paper unduly. The computed results will, however, be included in a table at the end of this paper.

#### ALKALI METALS.

Both photo-electric and thermionic experiments on the alkali metals are extremely difficult on account of the great susceptibility of these metals to contamination. While many attempts have been made to determine the frequencies of the photo-electric thresholds and also of the selective effects, the results obtained by the various investigators are very discordant. On the other hand, very few attempts have been made to study

<sup>1</sup> *Loc cit.*



the thermionic emission of electrons from these metals. Nevertheless, we must test the applicability of the present law with whatever experimental data we have at our disposal at present.

### 1. Sodium :—

Observers	$\lambda_m$	$\lambda_0 = \frac{3}{2}\lambda_m$
1 Pohl and Pringsheim <sup>1</sup>	320 $\mu\mu$ —340 $\mu\mu$	480 $\mu\mu$ —510 $\mu\mu$
Richardson and Compton <sup>2</sup>	360 $\mu\mu$	540 $\mu\mu$
Richtmeyer <sup>3</sup>	460 $\mu\mu$	690 $\mu\mu$

But according to Thomson's theory  $\lambda_m$  is 324 $\mu\mu$  which corresponds to a value 486 $\mu\mu$  only for  $\lambda_0$ . Thomson-Richardson law, therefore, appears to have failed in correctly representing the characteristic photo-electric behaviour of sodium. Such a conclusion would, however, be superficial. For this law is in good quantitative agreement with the photo-electric measurements on all other alkali-metals. It is conceivable, however, that sodium contains oscillators possessing natural frequencies of two or more particular values so that the emission might be maximum at two or more points, when the stimulating frequency might be greater or equal to the characteristic frequencies.

One could naturally suppose that the direct determination of the long wave-length-limits of sodium might lead to some decision on the point. But one is simply disappointed by the widely discordant result of the different investigators.

Observers.	$\lambda_0$
Richardson and Compton <sup>4</sup>	577 $\mu\mu$ —583 $\mu\mu$
Souder <sup>5</sup>	> 623.5 $\mu\mu$
Millikan <sup>6</sup>	680 $\mu\mu$

<sup>1</sup> Verb. d. Deutsch. Phys. Ges, XI, r. 1039, 1910.

<sup>2</sup> Phil. Mag. 26, 549, 1913.

<sup>3</sup> Phys. Rev, Vol. XXX, 3, 1910.

<sup>4</sup> Phil. Mag., 26, 549, 1913.

<sup>5</sup> Phil. Mag., 25, p. 576, 1912.

<sup>6</sup> Phys. Rev., Vol. VII, 1st series, 1916.

Observers.	$\lambda_0$
Richtmeyer <sup>1</sup>	598 $\mu\mu$ —633 $\mu\mu$ .

If one accepts Richardson and Compton's value 593 $\mu\mu$  for  $\lambda_0$ ,  $\phi_{\text{phot}}$  becomes 2.12 volts.

The only thermionic data on sodium are due to Fredenhaagen and Richardson. Fredenhaagen failed to remove gaseous contaminations and his results are, therefore, useless for a quantitative test of the present theory. Richardson's experiments on sodium are also not very reliable. He obtained thermionic currents of the order  $10^{-8}$  amperes per sq. cm. at 500°C. Calculated from his data,  $\phi_{\text{therm}}$  comes out to be 2.01 volts. The order of correspondence between the theory and the observations of the various investigators is not very unsatisfactory. Yet it appears as if this alkali has kept concealed in itself some mystery yet unrevealed.

2. *Cæsium*.—Very little is known about the photo-electric behaviour of this alkali. According to Cornelius's <sub>2</sub> observations  $\lambda_0$  is greater than 750 $\mu\mu$ . Pohl and Pringshein<sup>3</sup> gives the value 550 $\mu\mu$  for  $\lambda_m$  which corresponds to a value 825 $\mu\mu$  for  $\lambda_0$ . According to Thomson-Richardson law,

$$\lambda_0 = .9942 \times 10^{-8} \times \left( \frac{132.8}{1.87} \right)^{\frac{1}{2}} \text{ cmz}$$

$$= 838 \mu\mu$$

$$\phi_{\text{phot}} = 1.47 \text{ volts}$$

Calculated from Langmuir's <sup>4</sup> recent data for emission from cæsium,  $b$  is 15930 and hence  $\phi_{\text{therm}}$  is equal to 1.38 volts. The agreement between  $\phi_{\text{therm}}$  and  $\phi_{\text{phot}}$  for cæsium is quite good. The absence of any thermionic data for other alkali metals handicaps me in examining them in the light of the present theory.

<sup>1</sup> Phys. Rev., Vol. XXX, No. 3, 1910.

<sup>2</sup> Phys. Rev., 1913, Vol. 1, second series.

<sup>3</sup> Loc. cit.

<sup>4</sup> Science, 57, pp 58-60, Jan. 1923.

A summary of the computed values of  $\phi_{\text{therm}}$  and the characteristic photo-electric constants either calculated according to Thomson-Richardson law or directly observed, is given below for comparison.

TABLE VI.

Metallic elements	THERMIONIC		PHOTO-ELECTRIC.		RICHARDSON-THOMSON RULE.	
	$\phi_{\text{therm}}$ in volts.	$\lambda_0$ in $\mu\mu$	$\lambda_m$ in $\mu\mu$ (obs.)	$\lambda_0$ in $\mu\mu$ (obs.)	$\lambda_m \mu\mu$	$\lambda_0 = \frac{2}{3} \lambda_m \mu\mu$
Pt	4.18 (Suhrmann)	295.7		291 (Richardson)	197.3	296
	4.17 (Sehlichter)	296.2				
W	4.23 (Langmuir)	292.2	.	230 (Kelley)	205.0	307
	4.05 (Smith)	300.2				
Mo	3.93 (Langmuir)	315.1	.	.	215.3	323
Ta	3.82 (Suhrmann)	323.4	.	.	218.7	328
Th	2.74 (Langmuir)	451.1	.	.	304.7	457
Na	2.09 (Richardson)	614.9	{ 320-340 (Pohl, etc.) 460 (Richtmeyer)	583 (Richardson)	{ 324	486
				538-633 (Richtmeyer).		
K	..	...	440 (Pohl, etc.)	...	446	669
Rb	.	..	480 ditto		494	741
Cs	1.38 (Langmuir)	896	550 ditto	> 750 (Comelius)	559	838
C	4.52 (Langmuir)	274	.	255-260 (Hughes)	168-178	252-257
	4.51-4.97 (Pring and Parker)	250-275				

*Concluding remarks.*—It would be premature at present to pronounce any definite opinion on the question of identity between photo-electric and thermionic work functions, specially in view of the uncertainties in the determinations of the long wave-length-limits. The data collected in Table VI, however, points to a general correspondence between the two. The universal applicability of the Richardson-Thomson rule, used here empirically to a large number of metals, is probably doubtful. But it certainly indicates the possibility of a

theoretical estimation of the long-wave-length limits from the space-lattice arrangements of electrons in different metals.

The thermionic work-function  $\phi_-$  in volts may be looked upon as the sum of two potentials  $\mu_-$  and  $\psi_-$ .<sup>1</sup>  $\mu_-$  is the electron-affinity inside a metal, and is essentially related to the nature of electron-binding with atoms or atomic residues.  $\psi_-$  is the surface-potential of the metal and is due to the work which an electron has got to do in escaping from the surface of the metal against the force of attraction of its image-point which at a distance  $d$  from the surface is equal to  $\frac{\delta}{4d}$ .<sup>2</sup> It is, of course, implied that the concentration of the emitted electrons is so low that any potential difference arising out of their space-charge is negligible. If the emission becomes copious, the space-charge potential cannot be dismissed as being negligible.

Russel has pointed out that the ionisation potential of gases and vapours is a periodic function of the atomic number. One would, therefore, expect the same remark to apply to the ionisation potentials of elements in the condensed phase.<sup>3</sup> Now whatever view be taken of the thermionic work-function, the figures in column I of Table VI, appear to make it abundantly clear that the work-function  $\phi$  is a function of the atomic volume.

<sup>1</sup> W. Schottley, *Zeit*

<sup>2</sup> *Phys* 14, 63, 1923.

<sup>3</sup> *Astr. Phys. Journ*, Vol VI, 1922



## On the colours shown by "Nobili's Rings."

By

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### INTRODUCTION.

When a polished plate of platinum, silver or brass, connected with one pole of a battery is immersed horizontally in a suitable electrolytic solution and a vertical wire of platinum connected with the other pole is held in the solution about a millimetre distant from the plate, then on passing a strong current through the circuit so made, beautiful rings are formed upon the plate with the platinum point as the centre. Such rings were noticed first by Nobili<sup>1</sup> and since then they have been obtained by Schönbein<sup>2</sup> with a passive iron wire as the positive pole in a lead acetate solution and by Fechner<sup>3</sup> upon a silver plate using a solution of copper acetate and a zinc wire point as one electrode. Later on Becquerel<sup>4</sup> obtained the rings on a German silver plate. The rings obtained with copper sulphate solution were not much coloured, but those obtained employing other solutions showed beautiful colours, and Becquerel observed that the rings showed colours like Newton's rings in white light and from that similarity he proceeded to determine the diameter of the rings from the consideration of the current

<sup>1</sup> Nobili—Bibl. Univ 33, p. 302, 1826

Pogg Ann, 10, p. 392, 1827.

<sup>2</sup> Schönbein—Pogg Ann, 40, p. 421, 1837.

<sup>3</sup> Fechner—Schweigg Journ. 55, p. 442, 1829.

<sup>4</sup> Becquerel—Ann de chim et de phys (3) 13, p. 342, 1845 Archives l' El 4, p. 82.

density about the platinum electrode. His results were verified by Beetz<sup>1</sup> later on.

Although the phenomenon was observed so many years ago, yet no satisfactory explanation about the origin of such beautiful colours in those rings seems to have ever been attempted. The similarity of colour sequence in these rings to the white light Newton's rings, suggested the explanation that here also we had the phenomena of interference and the colours are due to the interference of light by thin films deposited upon the metal plate whose thickness diminished as one moved away from the centre, the point just below the vertical electrode.

The present author in a previous paper<sup>2</sup> made a complete study of the Colours shown by tempered metal surfaces. As the colours in the present instance have many properties in common with the colours shown by heated metal surfaces, it at once suggested that the underlying cause may be the same in both phenomena. In the present investigation, an attempt has been made to explain the colours from the stand point that the films deposited upon the metal plates for the formation of Nobili's rings during electrolysis are discontinuous and granular in structure and hence the colours must originate from the scattering of light by those granular particles upon a polished metal surface.

## 2. PRODUCTION OF NOBILI'S RINGS.

The proper metal plate for the production of rings is to be selected. In fact different metal plates have been employed by different investigators in connection with different solutions. The present author tried to get rings with saturated solutions of copper sulphate, lead sulphate and manganous sulphate and plates of brass, silver, copper

<sup>1</sup> Beetz—Pogg Ann 71, p 79, 1847.

" " 97, p 22, 1856.

<sup>2</sup> B. N. Chuckerbutti—Proc. of Ind. Assoc. for the Cultivation of Science, Vol. VII, Parts III and IV, 1922.

and aluminium. The rings are very beautifully obtained in cases where the metal plate is connected with the negative terminal of the battery.

In experiments with copper sulphate solution, the rings obtained upon a brass plate are almost colourless, there being dull-red rings of copper separated by brighter intervals. But some colouration is obtained, however, when sufficient time is allowed for the oxidation, in contact with air, of the liberated metal during the interval between the taking out of the plate from the solution and cleansing by tap water. Such colours are however formed only at places sufficiently removed from the centre because it is there that we should expect small particles not yet set upon the metal bed, whereas the layers near the centre are not affected at all. It was possible however to get an entire set of coloured rings in the case of copper sulphate solution and a negative plate of silver by allowing the current to pass for a very short time and then taking out the plate immediately. The succession of colour in such rings was from the centre outwards—dull-red, yellow, green, violet. The rings obtained with lead sulphate solution and a negative brass plate, however, surpass all description in gorgeousness of colour. About four or five complete rings were distinguishable. The arrangement of colours was from the centre outwards—dull-red, yellow, bluish-green, violet-red, green-yellow, blue and reddish violet. Similar coloured rings were also obtained with manganous sulphate solution and a negative brass plate.

In the case of negative aluminum plate in a copper sulphate solution, the alternate rings of metallic copper are beautifully seen against the whitish back-ground. But it requires rather a greater time for the formation of rings in this case than in the cases cited before. Attempts were also made with a copper plate. But in this case although the deposition was in alternate rings, the contrast was not good and moreover the rings were very near together.



The current to be employed in all these cases should be sufficiently high and the whole phenomenon is complete within 10 to 15 seconds. A feeble current gives only a deposit without formation of any definite rings. The current employed in all cases was about 2 amperes from a main of 220 volts.

For the best production of coloured rings it is essential that the metal surface should be highly polished. It is impossible to get the well-coloured rings with a rough surface, but only a nonuniform deposit is obtained. Another important point for success in these experiments is that the vertical electrode should be as near the plate as possible but never touching it. For, otherwise, although the other conditions might be satisfied, no rings are formed even if the current is passed for a sufficient time.

### 3. MICROSCOPIC OBSERVATION OF THE METAL PLATES.

That the structure formed upon the metal surface during electrolysis is not continuous but granular, can be seen at once if the plates be subjected to a microscopic study. The difficulty lies in the fact that the metal surface being in the background, the granules cannot properly be illuminated. The difficulty can, however, be overcome by employing light from a high candle power source incident very obliquely upon the plate. Beginning the observations from the centre of the ring system to the farther side, the variation in the nature of the structure in different parts is marvellously shown. At a distance are found the minute particles quite separate from one another but sometimes forming clusters. But as the centre of the system is approached little by little, the size of the particles also increases. It should be noted, however, that the regions of bigger particles are not quite free from the presence of smaller granules so common at the distance. It is possible to measure the size of the granules with the help of a micrometer eyepiece. Thus for the smallest

particles the diameter comes out to be  $275\mu\mu$  (or  $ka=1.35$ , where  $k=\frac{2\pi}{\lambda}$ ,  $a$  is the radius of the particle,  $\lambda$ =wave-length of light) and for the biggest particles obtained, the diameter comes out to be  $500\mu\mu$ . Thus the size of the particles obtained in the present circumstances is of the same order of magnitude as the particles formed upon a heated metal surface.<sup>1</sup>

#### 4. DETAILED STUDY OF THE PHENOMENA OBSERVED.

##### (A) *Colour and Polarisation of Reflected Light.*

If a beam of white light is allowed to fall upon the ring systems and the reflected light observed then, the colour and polarisation of the reflected light vary with the angle of incidence and the position of the ring, in a very remarkable way. On viewing the reflected light with the naked eye the reflected colours are most lively at or about normal incidence, and become less and less saturated as the obliquity of incidence is increased and, at very oblique incidence, it is impossible to distinguish the colours in the different rings, the proportion of white light reflected being very great.

On employing a nicol for observation it is found that at small obliquities only the last two rings are affected in colour and intensity as the nicol is rotated about its axis, but the rings near the centre show no appreciable change at all. At more oblique incidences, however, the colour of the rings near the centre show striking changes as the nicol is rotated from one position (namely, principal plane perpendicular to the plane of incidence) to the position normal to it. Thus, in the first position of the nicol the colours are vivid but less intense and in the second position their intensity increases but they become less strongly coloured. It is further to be noted that for oblique incidences the colours observed in the two positions of the nicol are complementary to each other.

<sup>1</sup> B. N. Chuckerbutti, *loc. cit.*, p. 80.

The arrangement of colours in the ring system observed in reflected white light incident normally, upon the Nobili's rings formed upon a brass plate with lead sulphate solution is as follows.

Centre—Dull red.

First ring—Yellow, bluish green.

Second ring—Green, Violet-red.

Third ring—Green yellow, blue, Reddish-violet.

*(B) Colour and Polarisation of the Scattered light.*

It is a very important feature of the deposits upon metal plates which give rise to Nobili's rings that they scatter light very profusely. As a general rule, it may be observed that the colour of the scattered light in directions near about that of the regularly reflected light is complementary to it. The behaviour of the scattered light for various angles of observation, when white light is incident normally, can be observed with a certain amount of exactitude, if the plate be mounted normally upon the table of a Cornu polarimeter fitted with an analyser and also polariser. The apparatus is essential in such experiments and also in other experiments on the polarisation of light. The observations may be divided under two heads as follows :—

(i) *Polarised White Light incident normally.*—When polarised white light is incident normally upon the rings, the scattered light in directions very near to the direction of the normal to the plate cannot be quenched in any position of the analysing nicol but the intensity shows fluctuation as the nicol is rotated through various positions. But at angles very near to the surface the colours can entirely be quenched by the analysing nicol but re-appear again on further rotating the nicol. In viewing with the naked eye, it is found that the colours in different rings take up different tints, as the angle of observation is changed.

(ii) *Unpolarised white light incident normally.*—In viewing with the naked eye in directions contiguous to the plane of the plate, the number of rings distinguishable is not very great but as the angle is increased most of the colours come to view. As one proceeds towards the normal to the plate the colours of the rings pass through several fluctuations and in directions near about the direction of the regularly reflected light, the colours in the rings are complementary to those of the scattered light.

The scattered light shows first traces of polarisation at an angle of about  $60^\circ$  with the normal. In that position the colour of the external big rings shows the complementary tint on rotating the analysing nicol through a right angle but the colours of the inner rings are not affected much. Then from that position as the direction of the surface of the plate is approached, the colour of all the rings changes remarkably on the rotation of the nicol.

## 5. EXPLANATION OF THE PHOTOGRAPHS.

The Photographs (Plate I) were obtained to show the complementary nature of the reflected and scattered light in certain directions. To obtain these, light from a 1,000 candle-power electric lamp after passage through a monochromator ( $\lambda=6260$  A. U.) was made to fall upon the plate containing the rings. Two such metal plates were used, namely, the brass plate showing the rings due to lead sulphate solution, and also the brass plate showing the rings due to copper sulphate solution. Figs. 1 and 2 give the photographs of the rings on the first metal plate by the regularly reflected light and the scattered light in a direction near about to that of the reflected light, respectively. Similarly, Figs. 3 and 4 show the rings due to copper sulphate solution in the reflected and scattered light respectively. On account of the feebleness of the scattered light, the negatives were not much dense even after an exposure for twelve hours. The contrast is thus

not very clear for rings sufficiently removed from the centre.

## 6. DISCUSSION AND CONCLUSION.

The similarity of the different observed facts in connection with the metal plates employed in the present case, with the metal-plate-colours obtained by heating, is quite apparent. The experiments in the present case however, could not be pushed further and all attempts for a quantitative study of the intensity of the scattered light and its verification according to the theory developed by the present author in the previous paper mentioned before, proved unsuccessful. The difficulty lies in the fact that the rings are so near together and the different colours are thus blended with one another that it is impossible to select a portion of moderate dimensions which would show uniform scattered colours due to the particles of similar dimensions. The method proved quite unsuitable for the present case and can only be used in cases where the entire metal surface is coloured uniformly giving the same tint. In spite of that, the complementary nature of the reflected and scattered light as shown by the photographs and the qualitative study of the reflected and scattered light at once suggest that the colour must be due to the granular deposition of particles liberated during electrolysis. As it is metallic copper which is deposited in case of copper sulphate solution, we get no colour except that of the metal itself. But in the other cases it is the oxide of the metal which is deposited and hence the root cause of the colours is identical with the case of heated metal surfaces.

(i) In the present paper an attempt has been made to explain the colours shown by Nobili's rings. All observed facts support the view that the colours must be due to the diffraction of light by the granular structure formed during electrolysis.

(ii) Photographs are given showing the complementary nature of the reflected and scattered light which fact supports the idea of Diffraction as the origin of the Colours.

The best thanks of the author are due to Prof. C. V. Raman who suggested this work.

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# The Polarisation of Resonance Radiation and the Duration of Excited State.<sup>1</sup>

By

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## INTRODUCTION.

According to Bohr, the emission of radiation from an atom is preceded by the transference of an electron from its normal stationary orbit to an orbit of higher energy and the radiation takes place during the return of the electron to its normal orbit. From his correspondence principle, the polarisation and intensity of light of a definite frequency emitted during any transition process can be co-ordinated with the configuration of the orbits and the amplitudes of the appropriate components of vibration in different directions. In the case of resonance radiation, the exciting agency is the electric vector in the incident light-wave, and, if the incident light is plane-polarised, we may expect that when just excited, the component of vibration corresponding to the transition would be greatest in the direction of the electric vector in the incident light. The polarisation of the emitted radiation would depend on the orientation of the plane of motion of the electron at the time of its return to the original orbit. When secondary radiation can be neglected, the circumstances that might alter the orientation and form of the orbits are (1) Perturbations due to internal or external fields of force and (2) Collisions with other atoms or molecules. If by reason of one or more of these causes, the orientations of the electron orbits have been rendered random before the quantum-jump takes place, the radiation would be unpolarised.

<sup>1</sup> Read before the Indian Science Congress—January, 1924. Revised August, 1924.



The recent experimental results of Professor R. W. Wood and Mr. A. Ellett<sup>1</sup> on the polarisation of the resonance radiation of the vapours of mercury and sodium in weak magnetic fields are of considerable interest in this connection. In the case of the resonance radiation  $2537\text{\AA}^\circ$  in mercury vapour at a pressure of the order of  $\cdot 0002$  mm., a field of  $1\cdot 5$  gauss applied in the direction of the magnetic vector of the incident light was sufficient to reduce the polarisation of the light emitted in that direction from 90 per cent. to about 10 per cent. Various interesting features of polarisation as the direction of the magnetic field was altered are recorded. A simple general explanation of the observed phenomena can be given by taking into account the Larmor precession of the approximately elliptic orbit of the electron round the direction of the magnetic field and the finite duration of the excited condition of the atom.

For convenience of reference, it is useful to summarise in a tabular form Wood's detailed observations which were made on sodium vapour at about  $180^\circ\text{C}$ . OX denotes the direction of the incident beam of plane polarised light and OY the direction of observation. When the direction of the electric vector of the incident light was parallel to OZ, the polarisation of the resonant light was 5 per cent. in zero field and it required a field of about 100 gauss parallel to OY to destroy the initial polarisation.

TABLE I.

Direction of Electric Vector in incident light	Direction of magnetic field (100 gauss)	Polarisation.
OZ	OY	Nil
OZ	OX	Strong (about 80 p. c.) with el. vector II OZ.
OZ	OZ	Strong with el. vector II OZ
OZ	$45^\circ$ with OZ in XZ plane	Nil
OY	zero field	Nil
OY	OX	Strong with el. vector II OZ.
OY	OZ	Strong with el. vector II OX.
OY	$45^\circ$ with OZ in XZ plane	Strong with el. vector $\perp$ field.

<sup>1</sup> Proc. Roy. Soc. A, Vol. 103, p. 896 (1923).

Results of the same general character were obtained with mercury vapour also, with the difference that the polarisation was much more pronounced and the various features came out with a much weaker field of about 2 gauss.

*Simple Theory of the Changes of Polarisation in a Magnetic Field.*

The effect of a magnetic field is to superpose on the motion of the electron a uniform rotation round the direction of the field, the frequency of rotation being  $\pm He/4\pi mc$ .<sup>1</sup> We shall take the simple case when the resonance radiation is completely polarised in the absence of the field, as is nearly the case in mercury vapour. When the incident light is plane-polarised with the electric vector parallel to OZ and the light is observed along OY, the application of a magnetic field either along OX or OZ would cause the light to be polarised along OZ, because the rotation round OX or OZ cannot contribute anything to the X-component. As the magnetic field is gradually turned from OX to OZ, the axis round which precession takes place would also turn round and it is easily seen by decomposing the vibrations parallel and perpendicular to the field that the percentage of polarisation would first diminish to zero and again increase. The minimum of polarisation can easily be shown to occur when the magnetic field makes an angle  $\theta$  with OX where  $\tan^2\theta = 1/2$ . This angle, which is nearly  $35^\circ$  differs appreciably from the  $45^\circ$  which Wood obtained with sodium vapour. When the electric vector is applied parallel to OY and the magnetic field is applied parallel to OX or OZ, the rotation of the orbits round the field would lead to strong polarisation, the stronger components being along OZ and OX respectively, and this will also be accompanied by an *increase* of intensity. All these results are in general agreement with Wood's observations.

<sup>1</sup> J. Larmor, *Phil. Mag.*, 44, 503 (1897).

We cannot, however, expect quantitative agreement with the theory outlined above except in the case where the atom shows normal Zeeman effect. With atoms like sodium which exhibit an anomalous Zeeman effect, the effect of the magnetic field would not be a simple rotation round the direction of the field.<sup>1</sup> The 2,537 line of mercury also does not show a normal effect, but its Zeeman separation is of the normal triplet type with a separation  $\frac{2}{3}$  times the normal value.

*Period of Precessional Rotation and Duration of  
Excited State.*

One interesting feature observed with mercury vapour was the gradual decrease of polarisation from 90 per cent. to 10 per cent. as the magnetic field along OY was increased from 0 to 1.3 gauss. The phenomenon admits of a simple explanation on the above theory. When the precessional rotation is very slow, most of the radiation would have taken place before the corresponding vibrations in the excited atoms have been deflected through an appreciable angle from OZ and the radiation would retain most of its initial polarisation. As the intensity of the field increases, the component of vibration along the original direction would diminish and that in a perpendicular direction would increase, until with large speeds of rotation the light would be completely unpolarised. Putting in numerical values, the period of precessional rotation  $4\pi mc/eH$  round the direction of the magnetic field is  $7 \times 10^{-7}/H$  sec, and according to the measurements of Wien<sup>2</sup> on the gradual decrease of intensity of the 2,537 line of mercury when positive rays are allowed to stream into a

<sup>1</sup> G. Breit (Phil Mag., May, 1924) has succeeded in explaining the leading features of the polarisation of resonance radiation in sodium vapour on the lines of the quantum-theory of anomalous Zeeman Effect.

"Molrefraction von Ionen und Molekülen in Lichte der Atomstruktur" by K. Fajan and G. Joos—Zeitschrift Für Physik, April, 1924, p. 1.

<sup>2</sup> Wien; Ann der Physik, 73, p. 483, 1924.

high vacuum, the intensity diminishes with time in the ratio<sup>1</sup>  $e^{-2\alpha t}$  where  $2\alpha = 1.02 \times 10^7 \text{ sec.}^{-1}$ . Let us consider a large number of atoms excited to resonance with vibrations parallel to OZ and rotated round the direction of the magnetic field OY with angular velocity  $\omega$ . The intensity of radiation from the atoms whose corresponding vibration directions make an angle  $\theta$  with OZ would be, on the average,  $a^2 e^{-2\alpha t}$  and the average amplitude would be  $ae^{-\alpha t}$  where  $t$  is the time required to turn through an angle  $\theta$  under the precessional rotation, and  $a$  is the amplitude of the corresponding vibration when  $t=0$ . Resolving along OZ and OX, squaring, and integrating over all atoms at different stages of radiation from  $t=0$  to  $t=\infty$ , we get

$$\frac{Z}{X} = \frac{\int_0^\infty e^{-2\alpha t} \cos^2 \omega t \, dt}{\int_0^\infty e^{-2\alpha t} \sin^2 \omega t \, dt}$$

where Z and X are the components of intensity with vibrations along OZ and OX respectively. The integrals are easily evaluated and give

$$\frac{Z}{X} = \frac{\omega^2 + 2\alpha^2}{\omega^2}.$$

Hence, the polarisation as observed along the Y axis is measured by

$$\frac{Z-X}{Z+X} = \frac{\alpha^2}{\omega^2 + \alpha^2}.$$

<sup>1</sup> It does not matter for our present purpose whether this exponential decrease in intensity is due to the rate of decrease in the number of quantum-jumps or whether it is due to an exponential decrease with time of each elementary process of radiation. For a discussion, see G. Mie; *Ann. der Physik*, 73, p. 195, 1924.

This shows a gradually decreasing polarisation as  $\omega$  is increased.

Substituting Wien's value of  $2a$  in our expression, we obtain a series of values for the polarisation for different intensities of the magnetic field. These have been plotted in Figure I. Wood's experimental values have also been plotted for comparison. The *course* of experimental values of the polarisation is well reproduced by the theoretical curve. It should be remembered that we have assumed perfect polarisation for zero field, while the experimental value was 90 per cent.

*Mean Interval between Molecular Collisions and Duration  
of Excited State.*

There is yet another direction from which we can get some information regarding the duration of emission. Wood has observed that the intensity and polarisation of resonance radiation in mercury vapour are affected by admixture with other gases.<sup>1</sup> The addition of helium or argon increases the intensity while the addition of air or hydrogen diminishes it, but in all cases, the effect of the addition is to diminish the polarisation. It is obvious that the effect of some of the collisions of an excited mercury atom with a molecule of hydrogen or of air is to prevent the radiation taking place. But not all collisions are deadly, as is shown by the increasing imperfection of polarisation on increase of pressure. We may take it that a collision would disturb the electron-orbit of the excited atom; when the disturbance is mild, the effect will only be to change the configuration of the orbit thus disturbing the polarisation and to give it a slow rotation which would slightly affect the frequency of the emitted radiation, and when the disturbance is intense, the radiation

of the proper frequency will altogether be prevented.<sup>1</sup> From the chemical behaviour of the molecules and their behaviour towards free electrons, we may expect that collisions with helium and argon would on the whole be mild and that they would get more and more intense in the order nitrogen, hydrogen and oxygen.

For the same mean interval between two collisions of a mercury atom with a gas molecule the effect on the polarisation of the resonance radiation would be less and less marked (and the destructive effect on the intensity more and more marked) as we proceed in the same order, for in the latter gases, only a smaller fraction of the excited atoms can stand the shock of a collision and yet retain the power to radiate.

The following table shows the changes of intensity and polarisation as the mean interval between two collisions is altered. The experimental data have been taken from Wood's paper. The mean interval between two collisions of a mercury atom with a gas molecule has been calculated from the formula

$$\frac{1}{t} = 2v_2 s_1; \quad \sqrt{\frac{\pi}{h} \left( \frac{1}{m_1} + \frac{1}{m_2} \right)}$$

(Jeans, *Dynamical Theory of Gases*, Second Edition, page 268) where  $v_2$  is the number of molecules of the gas per c.c.,  $s_1$  the sum of the radii of a mercury atom and of a gas molecule assuming them to be spherical, and  $m_1$  and  $m_2$  are the masses of a mercury atom and of a gas molecule respectively. The diameter of a mercury atom has been assumed to be  $3.2 \times 10^{-8}$  cm. as calculated from the atomic volume (Sommerfeld: *Atombau und spectral linien*, p. 122, 3rd edition). The diameter of the excited atom is probably greater than that of

<sup>1</sup> Klein and Rosseland's impact of the "second kind," *Zeit fur Physik*, 4, 46, 1921.

the normal one and the mean intervals given below too large on that account. The collisions of two mercury atoms with each other have been neglected as the vapour pressure of mercury was very small compared with the pressure of the added gases.

TABLE II

Gas	Pressure.	Mean interval between two collisions of a mercury atom with a gas molecule	Intensity on an arbitrary scale	Polarisation.
Argon	3 mm.	$6 \times 10^{-6}$ sec	5	Faint
	5 mm.	$3.6 \times 10^{-6}$ sec	10	Gone
Helium	2 mm.	$5 \times 10^{-6}$ sec	4	Faint
	6 mm.	$1.7 \times 10^{-6}$ sec	10	Gone
Air (0.8 N <sub>2</sub> + 0.2 O <sub>2</sub> )	0.65 mm.	$2.4 \times 10^{-7}$ sec	2.5	Strong
	4 mm.	$4 \times 10^{-6}$ sec	1.	Nearly Gone
	1 cm.	$1.6 \times 10^{-6}$ sec	0.5	Gone
Hydrogen	0.65 mm.	$9 \times 10^{-6}$ sec	1	Strong
	4 mm.	$1.5 \times 10^{-6}$ sec	0.5	Faint
	1 cm.	$0.8 \times 10^{-6}$ sec	0.2	A trace

When the added gas is helium or argon, the interpretation of polarisation is not simple inasmuch as Wood has found that when mixed with these gases, the mercury atom can be excited over a small range of frequencies lying on either side of the proper resonating frequency, and we cannot *assume* that this resonant radiation would be as polarised as that excited by the core of the line. The case of air also is not simple, because we have here two kinds of collisions, collisions with nitrogen molecules and collisions with oxygen molecules. Of these, the former may be expected to give rise to some unpolarised light while the latter will be more effective in

causing a radiationless transfer of the electron. In hydrogen, which causes the most marked change in intensity, we have, I think, the least complicated case.<sup>1</sup> When the mean interval between two collisions of a mercury atom with a hydrogen molecule is  $9 \times 10^{-8}$  sec, the polarisation is strong, but when the interval has come down to  $0.6 \times 10^{-8}$  sec, it has become a mere trace. From this, we can infer that a considerable part of the radiation has taken place between two collisions in the first case and that only a small part has taken place in the second. Assuming an exponential decrease of radiation with time, it is easy to calculate the average amount of radiation in the interval between two collisions. We have to remember that the time during which radiation can take place may be anything from 0 to  $t$  as the atom may be excited at any instant between two collisions. We thus get for the average fraction of energy radiated in the interval between two collisions<sup>2</sup>

$$R = 1 - \frac{1}{2at} \left( 1 - e^{-2at} \right)$$

Adopting Wien's value of  $2a$  for 2,536 line of mercury, we get the following values of  $R$  for various values of  $t$ .

TABLE III.

$t \times 10^8$ sec.	R
20	57
10	37
5	22
2	10
1	05

<sup>1</sup> It is of interest to note that Franck and Caro have found that collisions of excited mercury atoms with hydrogen molecules cause them to dissociate. Such a collision will certainly be radiationless. (Zeit. fur Physik, 11, 161, 1922.)

<sup>2</sup> Cario, Zeit. fur Physik 10, 135, 1922 Also Mie, loc cit



Of the unradiated part  $1-R$ , most of it would disappear on collision (being converted into other forms of energy) with the exception of a small fraction which would appear as unpolarised radiation. As  $T$  decreases, this fraction would increase and the polarised part  $R$  decrease, both causes tending to reduce the polarisation. Comparison of Table III with the figures for hydrogen in Table II show that this is sufficient to account for the leading features of the phenomenon.

The importance of obtaining further quantitative data in this field is obvious.

### *Summary.*

1. The changes of polarisation of the resonance radiation of the vapour of mercury in weak magnetic fields which have been studied by Wood and Ellett can be explained by taking into account the Larmor precession of the orbit of the electron round the direction of the magnetic field and the finite duration of the excited condition of the atom.

2. The duration of excited state required to explain the decrease of polarisation in mercury vapour resonance when a magnetic field is applied parallel to the direction of observation and perpendicular to the incident beam of light is consistent with Wien's determination of the same quantity.

The changes of intensity and polarisation of the resonance radiation when mercury vapour is mixed with other gases can also be explained by assuming that there is a finite time during which the atom remains in the excited state, and that the effect of a collision is either to destroy the radiation, or to disturb the polarisation so as to make its direction random.

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# K. R. RAMANATHAN

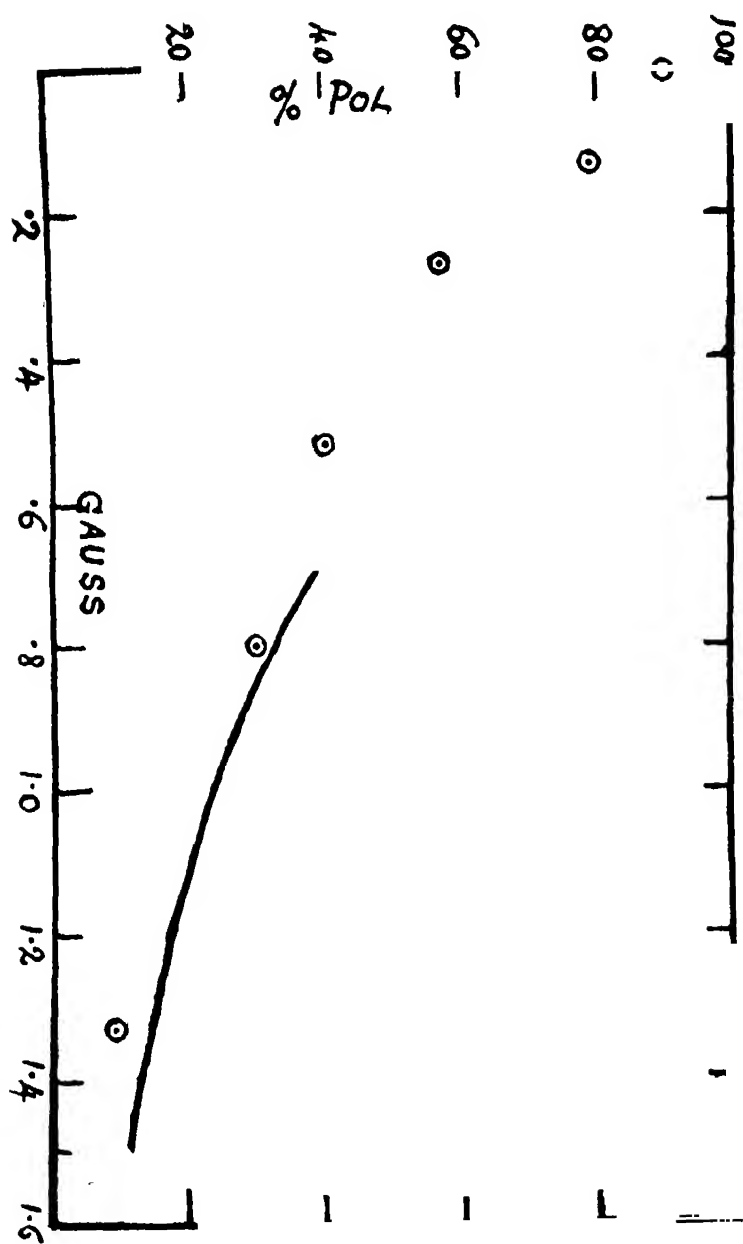


FIG. 1.



## Prevision of Earthquakes

By

HEMCHANDRA DAS-GUPTA, M.A., F.G.S.

It has been pointed out by Davison <sup>1</sup> that, though a prediction of earthquakes is not possible, we may attempt at their prevision, prediction being an accurate form of forecast, while prevision is only an approximate form of it. Dr. Davison has referred to two methods of prevision, both of them being applicable to the earthquakes of tectonic origin. One of them is due to Prof. Reid <sup>2</sup> and consists in erecting "a line of piers, say a kilometer apart, at right angles to the direction which a geological examination of the region, or past experience indicates the fault will take when the rupture occurs; and a careful determination, from time to time, of the directions of the lines joining successive piers, their differences of level, and the exact distance between them, would reveal any strains which might be developing along the region the line of piers crosses." The second method which we owe to Dr. Davison himself consists in carefully recording the fore-shocks and the after-shocks and depends on the hypothesis that "the increase in seismic activity along a known fault, and the tendency of uniformity in the distribution of that activity along the fault, may be heralds of the great crust-movements which cause disastrous earthquakes."<sup>3</sup> It is clear that Davison's method of prevision depends entirely on a careful recording of the fore-shocks and the after-shocks.

<sup>1</sup> Science Progress, Vol IX, pp 639 645, 1914-1915

<sup>2</sup> Reid, The California Earthquake of April 18, 1906, Report of the State Earthquake Investigation Commission, Vol. II, p. 81, 1910

<sup>3</sup> *Loc cit.*, p 645.

The Indian seismic tract No. 8 of Count F. de Montessus de Ballore comprising the Eastern Himalayas, Assam and Lower Bengal must have experienced a large number of shocks in the past as shown by the big shocks of (i) the 10th January, 1869, (ii) the 14th July, 1885, (iii) the 12th June, 1897 and (iv) the 8th July, 1918, but any systematic recording of the earthquake shocks was, evidently, seriously undertaken only after the great earthquake of 1897. The following figures have been published regarding the number of shocks recorded at Shillong<sup>1</sup> :—

Year	No. of shocks.
1897 (Aug.-Dec)                      ...	444
1898                      .                      .                      ...	486
1899                      .                      ...                      ...	246
1900                      ...                      ..                      ...	193
1901                      ..                      ...                      ..	164
1902                      .                      .                      .	135
1903-1908                      .                      .                      . .	No figures available.
1909-1913                      ...                      .                      .	16
1914-1917                      ...                      ...                      ...	114

These figures clearly show the evidence of renewed seismic activity during 1914-1917 which began during 1909-1913 and these shocks were but the fore-shocks or the fore-runners of the Srimangal earthquake of 1918. This earthquake originated in the seismic tract No. 8 and furnishes an evidence supporting Dr. Davison's method of earthquake prevision.

While dealing with the question of the prevision of the earthquakes in India all of which are of a tectonic origin, attention may be drawn to one important consideration. In the tectonic quakes the transfer of load from one part and its re-deposition in another part in such a way that a considerable amount of strain is set up along lines of comparative instability are the chief originating factors. So far as the

<sup>1</sup> These figures have been obtained from (i) Mem Geol. Surv. India, Vol. 30, pp. 1-102, 1900, (ii) Mem. Geol. Surv. Ind., Vol. 35, pp 117-150, 1903, and (iii) Proc. Asiatic Soc., Bengal, Vol. XIV, pp. xxi-xxiii, 1918.

Indian earthquakes are concerned the redistribution is carried on chiefly by running water, the transporting power being dependent upon various factors including its own volume. The amount of the available running water will depend primarily upon the amount of the rainfall and snowfall, while with an increase in the number of wet days, there is the chance of a decrease in the amount that may be lost by evaporation. The denudation work in an arid land is different from what prevails in a moist one and, on the Indian side of the Himalaya Mountains, in the work of denudation the most prominent part is played by rain and snow. It is, accordingly, not unlikely that in a country of tectonic earthquake, where the main work of denudation is carried on by the running water, there may be some sort of cause and effect relationship between the amount of rainfall and earthquake periodicity. In other words, it is not impossible that in such a country, after a number of years, the transfer and re-deposition of the load may be in such a proportion that a great strain is produced resulting in an earthquake due to the formation of a fault. A little consideration, however, shows that the question is not really so simple as it appears to be. Thus, for example, in the case of earthquakes of this nature it is quite likely that in the same tract the amount of the removed material need not always be approximately of the same load in all big earthquakes of tectonic origin. When the isostasy has been once established after the occurrence of a big earthquake, the crustal condition has certainly undergone some changes and, for the causation of the next earthquake, it is quite possible that the load, the redistribution of which may give rise to the shock, may be of a magnitude quite different from what was the origin of the preceding shock and eventually a time will come when the factors contributing towards the isostatic disturbance will disappear and there will be no earthquake. This mode of prevision is merely

a suggestion, but I think that it is worth testing. The idea is not a new one for I find that the late Prof. Knott was also inclined to believe in the same way <sup>1</sup> and the late Prof. Omori pointed out that in the whole of the Meiji area in Japan there was a remarkable coincidence between the frequency of the earthquakes and the amount of rain and snowfall.<sup>2</sup>

The tract No. 8 of Count F. de Montessus de Ballore is the most unstable portion of India and is also characterised by an abundance of rainfall. For a critical examination of the hypothesis outlined above, the seismic activity and the amount of rainfall of this region should be compared, but unfortunately from the incomplete earthquake and rainfall data nothing definite can be established at present regarding this relationship, but if careful observations are commenced now, and continued for some length of time, then we may arrive at some definite result.<sup>3</sup> It appears that each of the big shocks experienced in this area since 1869 occurred after a big interval during which disturbance of the isostatic condition was possible and in this disturbance, the denudation, transportation and deposition of the materials had certainly some share and they depended chiefly on the amount of rainfall. This hypothesis is, however, tenable only on the assumption that the earthquakes originate at a small distance from the surface of the earth.<sup>4</sup>

<sup>1</sup> Physics of earthquake phenomena (1908), p. 129.

<sup>2</sup> Nature, March 20, 1913, p. 65.

<sup>3</sup> Though a list of earthquakes was prepared and published by the late Dr. Oldham (Mem. Geol. Surv. Ind., Vol. XIX, pp. 103-215) dating from 893 or 894 A.D. no reliance can be put on the shocks chronicled as the data are extremely incomplete. Between the chronicled first and second shocks there is a gap of a little over 600 years.

<sup>4</sup> There seems to be at present a considerable difference of opinion regarding this point. Mr. Walker (Phil. Tran. Roy. Soc. Ser. A, Vol. 222, pp. 45-56, 1921) put the focus of an earthquake shock as low as 1250 km. though his results have been challenged by Dr. Banerjee (Nature, Jan. 26, p. 108, 1922). In a paper read before the Geological Society of London (Q. J. G. S. pp. 231-236, 1923.) Mr. R. D. Oldham has come to the conclusion that the ultimate origin of the earthquake of the 7th August, 1895, in Northern Italy, must have been of the order of 100 miles or more

# On the Motion Generated in a Viscous Liquid by the Translation of Certain Quartic Cylinders.

BY

SUBODH CHANDRA MITRA, M.A.

## INTRODUCTION.

1. It was first pointed out by Sir G. Stokes<sup>1</sup> that the two-dimensional motion of a circular cylinder with uniform velocity is impossible, when the equations of motion are simplified by the neglect of the "inertia terms." The explanation given by him suggests that the problem is insoluble for a cylinder of any form, if the "inertia terms" are neglected.

In a recent paper,<sup>2</sup> published in the proceedings of the Royal Society, an imperfect solution of the problem, when the moving body is an elliptic cylinder is given. Here the inertia terms are neglected, the condition of no tangential slipping at the surface is satisfied, but the velocity at infinity in one direction is infinite, which is contrary to experience.

In the present paper I have investigated the motion of cylinders whose cross-sections are

- (i) the inverse of an ellipse, and
- (ii) the elliptic limaçon.

<sup>1</sup> Stokes, 'Mathematical and Physical Papers,' Vol 3, p. 65.

<sup>2</sup> A. Berry and Miss L. M. Swain—'On the Steady Motion of a Cylinder through Infinite Viscous Fluid,' Proc. Roy. Soc., Series A, Vol. 102, No. 719, p. 766



It is seen that the condition of no slipping is satisfied at the surface exactly; the velocity vanishes at infinity; it is everywhere finite and continuous and last of all a definite value for the resistance is obtained.

The motion of the cylinder whose cross-section is an elliptic limacon, parallel to the axis of  $y$  (*i.e.*, in a direction perpendicular to the line of foci) presents difficulties with regard to continuity of motion along the double lines  $\eta=0$ . The treatment of this case is reserved for a subsequent communication.

## SECTION I.

### THE INVERSE OF AN ELLIPSE.

#### 2. *The Transformation.*

Let

$$x+iy=c \sec (\xi+i\eta).$$

Then

$$cx/r^2 = \cosh \eta \cos \xi$$

$$cy/r^2 = \sinh \eta \sin \xi$$

$$2c^2/r^2 = \cosh 2\eta + \cos 2\xi.$$

and

$$h^2 = \left( \frac{d\xi}{dx} \right)^2 + \left( \frac{d\xi}{dy} \right)^2.$$

$$= \left( \frac{d\eta}{dx} \right)^2 + \left( \frac{d\eta}{dy} \right)^2$$

$$= (\cosh 2\eta + \cos 2\xi)^2 / 2c^2 (\cosh 2\eta - \cos 2\xi).$$

The curves  $\xi=\alpha$  and  $\eta=\beta$  are the inverse of a family of confocal hyperbolæ and ellipses.

3. *The Stream-Function.*

When the inertia terms are neglected, the stream-function  $\psi$  for two-dimensional motion satisfies the equation

$$\nabla^4 \psi = 0.$$

where  $\nabla^2$  has the usual meaning.

To find a solution, let us write

$$\begin{aligned}\psi &= H_1 \sin \xi + H_2 \sin \xi / (\cosh 2\eta + \cos 2\xi) \\ &= \psi_1 + \psi_2\end{aligned}$$

where  $H_1$  and  $H_2$  are functions of  $\eta$  alone.

Then

$$2c^2 \nabla^2 \psi_1 = (H_1'' - H_1) \frac{(\cosh 2\eta + \cos 2\xi)^2}{(\cosh 2\eta - \cos 2\xi)} \sin \xi$$

Operating on both sides by  $\delta^2$  which stands for

$$\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2},$$

we have

$$\begin{aligned}2c^2 \delta^2 \nabla^2 \psi_1 &= \frac{\sin \xi}{(\cosh 2\eta - \cos 2\xi)^2} [(4P - P'') \cos^2 2\xi \\ &\quad - (P'' \cosh 2\eta + 12P' \sinh 2\eta + 20P \cosh 2\eta) \cos^2 2\xi \\ &\quad + \{(P'' - 4P) \cosh^2 2\eta + 16P - 8 \sinh 2\eta \times \\ &\quad (P' \cosh 2\eta + 2P \sinh 2\eta)\} \cos 2\xi + (P'' \cosh 2\eta \\ &\quad + 4P' \sinh 2\eta + 4P \cosh 2\eta) \cosh^2 2\eta + 32P \cosh 2\eta \\ &\quad - P (\cosh 2\eta + \cos 2\xi)^2 (\cosh 2\eta - \cos 2\xi) \\ &\quad - 4P (1 + \cos 2\xi) (\cosh 2\eta + \cos 2\xi) (8 \cosh 2\eta - \cos 2\xi)]\end{aligned}$$

where  $P$  is written for  $H_1'' - H_1$ .

Similarly

$$2c^2 \nabla^2 \psi_1 = \frac{\sin \xi}{(\cosh 2\eta - \cos 2\xi)} [H_1'' (\cosh 2\eta + \cos 2\xi) - 4H_1' \sinh 2\eta + H_1 (3 \cosh 2\eta + \cos 2\xi)].$$

therefore

$$\begin{aligned} 2c^2 \delta^2 \nabla^2 \psi_1 = & \frac{\sin \xi}{(\cosh 2\eta - \cos 2\xi)} [H_1' (\cosh^2 2\eta - \cos^2 2\xi) \\ & - 8H_1''' \sinh 2\eta \cos 2\xi + 16H_1'' \cosh 2\eta (1 + \cos 2\xi) \\ & - H_1'' (\cosh^2 2\eta - \cos^2 2\xi) - 4H_1''' \sinh 2\eta - (\cosh 2\eta - \cos 2\xi) \\ & - 16H_1'' (1 - \cosh 2\eta \cos 2\xi) + 16H_1' \sinh 2\eta (1 + \cos 2\xi) \\ & + 4H_1' \sinh 2\eta (\cosh 2\eta - \cos 2\xi) + 3(H_1'' - H_1) (\cosh 2\eta - \cos 2\xi)^2 \\ & + 2H_1'' (1 + \cos 2\xi) (\cosh 2\eta - \cos 2\xi) - 8H_1' \sinh 2\eta (1 + \cos 2\xi) \\ & - 8H_1 (\cosh 2\eta \cos 2\xi - 1) - 2H_1 (1 + \cos 2\xi) (\cosh 2\eta - \cos 2\xi) \\ & + 2H_1'' (\cosh 2\eta - \cos 2\xi) - 8H_1' \sinh 2\eta \\ & + 8H_1 (\cosh 2\eta + \cos 2\xi) - 8H_1 (1 + \cos 2\xi) \\ & - 2H_1 (\cosh 2\eta - \cos 2\xi)]. \end{aligned}$$

Adding  $\delta^2 \nabla^2 \psi_1$  and  $\delta^2 \nabla^2 \psi_2$  and equating to zero the co-efficients of the several powers of  $\cos 2\xi$ , we are led to the following equations.

$$P'' - 9P = 0 \quad \dots (1)$$

$$\begin{aligned} (P'' \cosh 2\eta + 12P' \sinh 2\eta + 20P \cosh 2\eta) - P \cosh 2\eta \\ + 4P(2 \cosh 2\eta - 1) + H_1' - 2H_1'' + H_1 = 0, \quad \dots (2) \end{aligned}$$

$$\begin{aligned} \{ (P'' - 4P) \cosh^2 2\eta + 16P - 8 \sinh 2\eta (P' \cosh 2\eta + 2P \sinh 2\eta) \} \\ - P \cosh^2 2\eta - 4P(3 \cosh^2 2\eta + 2 \cosh 2\eta) - 4H_1''' \sinh 2\eta \\ + 4H_1'' \cosh 2\eta + 4H_1' \sinh 2\eta - 4H_1 \cosh 2\eta \\ - 4H_1'' + 4H_1 = 0, \quad \dots (3) \end{aligned}$$

$$\begin{aligned}
& \cosh^2 2\eta (P'' \cosh 2\eta + 4P' \sinh 2\eta + 4P \cosh 2\eta) + 32P \cosh 2\eta \\
& - P \cosh^2 2\eta - 12P \cosh^2 2\eta + H_2'' \cosh^2 2\eta - 4H_2''' \sinh 2\eta \cosh 2\eta \\
& + 4H_2' \sinh 2\eta \cosh 2\eta + H_2''(2 \cosh^2 2\eta - 4 \cosh 2\eta) \\
& + H_2(4 \cosh 2\eta - 3 \cosh^2 2\eta) = 0.
\end{aligned} \quad \dots (4)$$

Solving we get

$$P = A \cosh 3\eta + B \sinh 3\eta.$$

Therefore

$$\begin{aligned}
H_1 &= \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \\
H_2 &= -\frac{1}{8}(A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{8}(A \cosh 3\eta \\
&+ B \sinh 3\eta) + E \cosh \eta + F \sinh \eta + G \eta \cosh \eta + H \eta \sinh \eta.
\end{aligned}$$

Substituting in the two equations (3) and (4) we get

$$G = 0$$

The stream-function can therefore be written in the form

$$\begin{aligned}
\psi &= \left\{ \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \right\} \sin \xi \\
&+ \left\{ -\frac{1}{8}(A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) \right. \\
&\left. + E \cosh \eta + F \sinh \eta + H \eta \sinh \eta \right\} \frac{\sin \xi}{(\cosh 2\eta + \cos 2\xi)}.
\end{aligned}$$

Let us suppose that the cylinder is moving along the axis of  $x$  with velocity  $U$  and that its cross-section is given by  $\eta = \beta$ .

If we write

$$u = -\frac{\partial \psi}{\partial y}, \quad v = \frac{\partial \psi}{\partial x}$$

then since at the boundary of the cylinder

$$u = U, \quad v = 0,$$

the boundary conditions are, when  $\eta = \beta$

$$\begin{aligned}
\frac{\partial \psi}{\partial \xi} &= -2cU \frac{\sinh \beta}{(\cosh 2\beta + \cos 2\xi)} \left\{ \cos \xi + \frac{2 \sin \xi \sin 2\xi}{(\cosh 2\beta + \cos 2\xi)} \right\} \\
\frac{\partial \psi}{\partial \eta} &= -2cU \frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)} \left\{ \cosh \beta - \frac{2 \sinh \beta \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)} \right\} \quad (a)
\end{aligned}$$

But from the expression for the stream-function, we have, when  $\eta = \beta$

$$\begin{aligned} \frac{\partial \psi}{\partial \xi} = & \left\{ \frac{1}{4}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta \right. \\ & + D \sinh \beta \} \cos \xi + \left\{ -\frac{1}{8}(A \cosh 5\beta + B \sinh 5\beta) \right. \\ & + \frac{1}{8}(A \cosh 3\beta + B \sinh 3\beta) + E \cosh \beta + F \sinh \beta \\ & + H\beta \sinh \beta \} \left\{ \frac{\cos \xi}{(\cosh 2\beta + \cos 2\xi)} + \frac{2 \sin \xi \sin 2\xi}{(\cosh 2\beta + \cos 2\xi)^2} \right\} \\ \frac{\partial \psi}{\partial \eta} = & \left\{ \frac{1}{8}(A \sinh 3\beta + B \cosh 3\beta) + C \sinh \beta + D \cosh \beta \right\} \times \\ & \sin \xi + \left\{ -\frac{1}{8}(A \sinh 5\beta + B \cosh 5\beta) + \frac{1}{8}(A \sinh 3\beta \right. \\ & + B \cosh 3\beta) + E \sinh \beta + F \cosh \beta + H(\sinh \beta \\ & + \beta \cosh \beta) \left. \frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)} - 2 \left\{ -\frac{1}{8}(A \cosh 5\beta + B \sinh 5\beta) \right. \right. \\ & + \frac{1}{8}(A \cosh 3\beta + B \sinh 3\beta) + E \cosh \beta + F \sinh \beta + H\beta \sinh \beta \} \times \\ & \left. \left. \frac{\sin \xi \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)^2} \right\} \right\} \end{aligned} \quad (b)$$

From (a) and (b) we are led to the following equations—

$$\frac{1}{4}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta = 0 \quad \dots (5)$$

$$\begin{aligned} & -\frac{1}{8}(A \cosh 5\beta + B \sinh 5\beta) + \frac{1}{8}(A \cosh 3\beta + B \sinh 3\beta) \\ & + E \cosh \beta + F \sinh \beta + H\beta \sinh \beta = -2cU \sinh \beta \quad \dots (6) \end{aligned}$$

$$\frac{1}{8}(A \sinh 3\beta + B \cosh 3\beta) + C \sinh \beta + D \cosh \beta = 0 \quad \dots (7)$$

$$\begin{aligned} & -\frac{1}{8}(A \sinh 5\beta + B \cosh 5\beta) + \frac{1}{8}(A \sinh 3\beta \\ & + B \cosh 3\beta) + E \sinh \beta + F \cosh \beta + H(\sinh \beta \\ & + \beta \cosh \beta) = -2cU \cosh \beta. \quad \dots (8) \end{aligned}$$

The orthogonal components of velocity are

$$-h \frac{\partial \psi}{\partial \xi} \quad \text{and} \quad h \frac{\partial \psi}{\partial \eta}.$$

At an infinite distance from the boundary,

$$\eta = \delta\eta \quad \text{and} \quad \xi = \frac{\pi}{2} - \delta\xi,$$

$$\cosh 2\eta + \cos 2\xi = 2(\delta\eta^2 + \delta\xi^2).$$

In order that

$$h \frac{\partial \psi}{\partial \xi}$$

may vanish at infinity, the expression

$$\begin{aligned} & \left\{ -\frac{1}{16}(A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{16}(A \cosh 3\eta + B \sinh 3\eta) \right. \\ & \left. + E \cosh \eta + F \sinh \eta + H\eta \sinh \eta \right\} \end{aligned}$$

must be of the second order of small quantities.

This requires that

$$E=0, \quad -\frac{1}{8}B + F=0 \quad \dots \quad (\text{v})$$

In order that

$$h \frac{\partial \psi}{\partial \eta}$$

may vanish at infinity the numerator of the expression

$$\begin{aligned} & \frac{1}{2} \left\{ -\frac{1}{16}(A \sinh 5\eta + B \cosh 5\eta) + \frac{1}{16}(A \sinh 3\eta \right. \\ & \left. + B \cosh 3\eta) + E \sinh \eta + F \cosh \eta + H(\sinh \eta \right. \\ & \left. + \eta \cosh \eta) \right\} - \frac{\sinh 2\eta}{(\cosh 2\eta + \cos 2\xi)} \left\{ -\frac{1}{16}(A \cosh 5\eta \right. \\ & \left. + B \sinh 5\eta) + \frac{1}{16}(A \cosh 3\eta + B \sinh 3\eta) + E \cosh \eta \right. \\ & \left. + F \sinh \eta + H\eta \sinh \eta \right\} \end{aligned}$$

must be of the third order of small quantities.

We then get the equations

$$E=0, -\frac{1}{8}B+F=0;$$

which are identical with the equations obtained above in (9).

At a point near the foci,

$$\eta=\delta\eta, \xi=\delta\xi \text{ or } \pi-\delta\xi,$$

$$h=c^{-1}(\delta\eta^2+\delta\xi^2)^{-\frac{1}{2}}$$

$$\text{and } \cosh 2\eta + \cos 2\xi = 2$$

In order that the velocity at this point may be finite, the expression

$$\begin{aligned} & \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \\ & + \frac{1}{8}\left\{-\frac{1}{16}(A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{16}(A \cosh 3\eta + B \sinh 3\eta) \right. \\ & \left. + E \cosh \eta + F \sinh \eta + H \eta \sinh \eta\right\} \end{aligned}$$

must be of the first order of small quantities.

This gives the additional equation

$$\frac{1}{8}A + C = 0. \quad \dots (10)$$

Solving the equations (5), (6), (7), (8), (9) and (10) we have

$$A = -8C = \frac{4cU}{\beta}.$$

$$B = 8F = -\frac{4cU}{\beta} \cosh 2\beta.$$

$$D = \frac{cU}{2\beta} \frac{(\cosh 2\beta + 2)}{(\cosh 2\beta - 1)} \tanh \beta.$$

$$H = -\frac{2cU}{\beta}$$

Whence we get the equation

$$A + 2H = 0 \quad \dots (11)$$

*The Continuity of Motion.*

4. If the motion is continuous along the double lines  $\eta=0$ , the derivatives of  $\psi$  will either vanish when  $\eta=0$ , or change sign in passing from one side to the other. Now from (b) it is seen that

$$\frac{\partial \psi}{\partial \xi} = 0$$

when we write  $\eta=0$  instead of  $\eta=\beta$  in (b), by virtue of the equations (9) and (10).

$\frac{\partial \psi}{\partial \eta}$  is easily seen to change sign when we write  $2\pi - \xi$  or  $-\xi$  for  $\xi$ .

Hence the motion is continuous along the line  $\eta=0$ , extending from the points  $(x = \pm c, y=0)$  to infinity. It can also be shown that the vorticity is finite everywhere. Further if  $u, v$  be the velocities parallel to the axes of  $x$  and  $y$  respectively, then it can be shown that the velocity-gradients, viz.,

$$\frac{\partial u}{\partial x}, \quad \frac{\partial u}{\partial y}$$

etc., are finite at all points.

*The Pressure.*

5. We know that  $\mu \nabla^2 \psi$  and  $p$  are conjugate functions.

$$\begin{aligned} \mu \nabla^2 \psi = \frac{\mu}{2c^2} \left[ A \left\{ -\frac{1}{3} \sin 3\xi \cosh 3\eta - \frac{1}{3} \sin \xi \cosh \eta \right. \right. \\ \left. \left. + \frac{2 \sin \xi \cosh \eta}{(\cosh 2\eta - \cos 2\xi)} \right\} + B \left\{ -\frac{1}{3} \sin 3\xi \sinh 3\eta \right. \right. \\ \left. \left. - \frac{1}{3} \sin \xi \sinh \eta \right\} + H \left\{ -2 \sin \xi \cosh \eta + \frac{4 \sin \xi \cosh \eta}{(\cosh 2\eta - \cos 2\xi)} \right\} \right]. \end{aligned}$$



Making use of equation (11), we find

$$p = \frac{\mu}{2c^2} \left[ A \left\{ -\frac{1}{2} \cos 3\xi \sinh 3\eta - \frac{1}{2} \cos \xi \sinh \eta \right\} \right. \\ \left. + B \left\{ -\frac{1}{2} \cos 3\xi \cosh \eta - \frac{1}{2} \cos \xi \cosh \eta \right\} \right. \\ \left. - 2H \cos \xi \sinh \eta \right] + \Pi_0.$$

where  $\Pi_0$  is the pressure at infinity.

It is at once clear that the pressure is finite everywhere.

### *The Resistance.*

6. The rates of elongation of the shear are given by

$$e = -f = \frac{1}{2} \left( \frac{\partial h^2}{\partial \xi} \frac{\partial \psi}{\partial \eta} + \frac{\partial h^2}{\partial \eta} \frac{\partial \psi}{\partial \xi} \right) + h^2 \frac{\partial^2 \psi}{\partial \xi \partial \eta}.$$

$$*r = h^2 \left( \frac{\partial^2 \psi}{\partial \eta^2} - \frac{\partial^2 \psi}{\partial \xi^2} \right) + \frac{\partial h^2}{\partial \eta} \frac{\partial \psi}{\partial \eta} - \frac{\partial h^2}{\partial \xi} \frac{\partial \psi}{\partial \xi}$$

when  $\eta = \beta$ .

$$2c^2 \frac{\partial h^2}{\partial \xi} = -2 \sin 2\xi (\cosh 2\beta + \cos 2\xi) \frac{(3 \cosh 2\beta - \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)^2}$$

$$2c^2 \frac{\partial h^2}{\partial \eta} = 2 \sinh 2\beta (\cosh 2\beta + \cos 2\xi) \frac{(\cosh 2\beta - 3 \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)^2}.$$

$$\frac{\partial^2 \psi}{\partial \xi \partial \eta} = 2cU \sinh \beta \left\{ \frac{2 \cos \xi \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)^2} \right.$$

$$\left. + \frac{8 \sin \xi \sin 2\xi \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)^2} - (2cU \cosh \beta) \times \right.$$

$$\left. \left\{ \frac{\cos \xi}{(\cosh 2\beta + \cos 2\xi)} + \frac{2 \sin \xi \sin 2\xi}{(\cosh 2\beta + \cos 2\xi)^2} \right\} \right\}.$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = -2cU \sinh \beta \left\{ -\frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)} + 4 \frac{\sin 3\xi}{(\cosh 2\beta + \cos 2\xi)^2} \right. \\ \left. + 8 \frac{\sin \xi \sin^2 2\xi}{(\cosh 2\beta + \cos 2\xi)^3} \right\}.$$

$$\frac{\partial^2 \psi}{\partial \eta^2} = L(\beta) \sin \xi + M(\beta) \frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)}$$

$$+ 8cU \frac{\sinh 3\beta \sin \xi}{(\cosh 2\beta + \cos 2\xi)^2} - 16cU \frac{\sinh \beta \sinh^2 2\beta \sin \xi}{(\cosh 2\beta + \cos 2\xi)^3}.$$

where

$$L(\beta) = \frac{1}{8}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta.$$

$$M(\beta) = -\frac{25}{16} \left( A \cosh 5\beta + B \sinh 5\beta \right)$$

$$+ \frac{9}{16} \left( A \cosh 3\beta + B \sinh 3\beta \right) + F \sinh \beta$$

$$+ H(2 \cosh \beta + \beta \sinh \beta)$$

and

$$\frac{\partial \psi}{\partial \xi}, \quad \frac{\partial \psi}{\partial \eta}$$

are given by (a).

substituting we find  $e=f=0$ .

$$\gamma = \left[ \frac{L(\beta)}{2c^2} \frac{(\cosh 2\beta + \cos 2\xi)^2}{(\cosh 2\beta - \cos 2\xi)} \sin \xi \right. \\ \left. + \frac{M(\beta)}{2c^2} \frac{(\cosh 2\beta + \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)} \sin \xi - 8 \frac{U}{c} \frac{\sinh \beta \sin \xi}{(\cosh 2\beta - \cos 2\xi)} \right. \\ \left. + 4 \frac{U}{c} \frac{(\sinh 3\beta \sin \xi + \sinh \beta \sin 3\xi)}{(\cosh 2\beta - \cos 2\xi)} \right. \\ \left. - 7 \frac{U}{c} \frac{\sinh \beta (\cosh 2\beta + \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)} \sin \xi \right].$$

The resistance on the cylinder is given by

$$R = \int \left( p \frac{dy}{ds} - W \frac{ds}{ds} \right) ds$$

where  $W = \mu\gamma$ , and the integration being taken round the boundary of the curve.

Integrating,

$$\begin{aligned} R &= -\pi \frac{\mu}{c} \cosh \beta \left\{ I_1(\beta) + M(\beta) + 2cU \sinh \beta \right\} \\ &\quad - 2\pi \frac{\mu}{c} \sinh \beta \left\{ \frac{3}{4} \left( A \sinh 3\beta + B \cosh 3\beta \right) \right. \\ &\quad \left. + \frac{3}{4} \left( A \sinh 5\beta + B \cosh 5\beta \right) - H \sinh \beta \right\}. \\ &= 4\pi\mu U/\beta, \end{aligned}$$

or restoring the values of the constants.

It is remarkable that the resistance is independent of  $\sigma$ .

The motion parallel to the axis of  $y$  can be obtained in an exactly similar manner.

## SECTION II.

### ELLIPTIC LIMAÇON.

#### 7. *The transformation.*

If

$$\xi + i\eta = 2 \sec^{-1} \sqrt{\frac{x + iy}{2c}},$$

then

$$4cx/r^2 = 1 + \cosh \eta \cos \xi,$$

$$4cy/r^2 = \sinh \eta \sin \xi.$$

$$r = 4c/(\cosh \eta + \cos \xi).$$

and

$$h^2 = \frac{1}{16c^2} \frac{(\cosh \eta + \cos \xi)^2}{(\cosh \eta - \cos \xi)^2}$$

The curves  $\eta = \text{constant}$  are elliptic limaçons, while the curves  $\xi = \text{constant}$  are hyperbolic limaçons.

### 8. *The Current-function.*

To investigate the motion parallel to the axis of  $x$  (i.e., the line joining the foci), let us assume

$$\begin{aligned} \psi &= H_1 \sin \xi + H_2 \frac{\sin \xi}{(\cosh \eta + \cos \xi)} + H_3 \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2}, \\ &= \psi_1 + \psi_2 + \psi_3 \end{aligned}$$

where  $H_1$ ,  $H_2$  and  $H_3$  are functions of  $\eta$  alone.

Then

$$16c^2 \nabla^2 \psi_1 = \sin \xi \frac{(\cosh \eta + \cos \xi)^2}{(\cosh \eta - \cos \xi)} (H_1'' - H_1).$$

Operating as before by  $\delta^2$ , we have

$$\begin{aligned} 16c^2 \delta^2 \nabla^2 \psi_1 &= \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2} \left[ (\cosh \eta + \cos \xi)^2 \times \right. \\ &\quad \{ 2(\cosh 2\eta + \cos 2\xi - 8 \cosh \eta \cos \xi + 8) P \\ &\quad + 4 \sinh \eta (\cosh \eta - 2 \cos \xi) P' + (\cosh^2 \eta - \cos^2 \xi) P'' \\ &\quad \left. - 4(2 \cosh \eta - \cos \xi) \cos \xi P - (\cosh^2 \eta - \cos^2 \xi) P \} \right]. \end{aligned}$$

where

$$P = H_1'' - H_1$$

similarly

$$\begin{aligned} 16c^2 \nabla^2 \psi_2 &= \frac{\sin \xi}{(\cosh \eta - \cos \xi)} \left[ (\cosh \eta + \cos \xi)^2 H_2'' \right. \\ &\quad \left. - 2 \sinh \eta (\cosh \eta + \cos \xi) H_2' \right] \end{aligned}$$

Therefore

$$16c^2 \delta^2 \nabla^2 \psi_s = \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2} \left[ (\cosh^2 \eta - \cos^2 \xi) \times \right. \\
\{ (\cosh \eta + \cos \xi) H_s' + 2 \sinh \eta H_s''' + (\cosh \eta - \cos \xi) H_s'' \} \\
+ 4(\cosh \eta + \cos \xi) H_s'' - 4 \sinh \eta \cos \xi \{ (\cosh \eta + \cos \xi) H_s''' \\
+ \sinh \eta H_s'' \} + 4 \cosh \eta (1 - \cos^2 \xi) H_s'' \\
- 2 \sinh \eta \{ (\cosh^2 \eta - \cos^2 \xi) H_s''' - 4 \sinh \eta \cos \xi H_s'' \} \\
- 8 \sinh \eta H_s' - 4 \cosh \eta \{ (\cosh^2 \eta - \cos^2 \xi) H_s'' \\
- 2 \sinh \eta \cos \xi H_s' \} - 2 \sinh \eta (\cosh^2 \eta - \cos^2 \xi) H_s' \\
- 2(\cosh \eta + \cos \xi) (3 \cosh \eta - \cos \xi) \cos \xi H_s'' \\
+ 8 \sinh \eta \cosh \eta \cos \xi H_s' - (\cosh \eta + \cos \xi)^2 (\cosh \eta - \cos \xi) H_s' \\
\left. + 2 \sinh \eta (\cosh^2 \eta - \cos^2 \xi) H_s' \right]$$

Also

$$16c^2 \nabla^2 \psi_s = \frac{\sin \xi}{(\cosh \eta - \cos \xi)} \left[ \{ (\cosh \eta + \cos \xi) H_s'' \right. \\
- 4 \sinh \eta H_s' + 4(\cosh \eta - \cos \xi) H_s + 4 \cos \xi H_s \\
\left. - (\cosh \eta - \cos \xi) H_s \} \right].$$

Therefore

$$16c^2 \delta^2 \nabla^2 \psi_s = \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2} \left[ (\cosh^2 \eta - \cos^2 \xi) H_s' + \right. \\
- 4 \sinh \eta - \cos \xi H_s''' + 4 H_s'' - 4 \sinh \eta (\cosh \eta - \cos \xi) H_s''' \\
- 8(1 - \cosh \eta \cos \xi) H_s'' + 4(\cosh \eta - \cos \xi)^2 H_s'' \\
+ 8 \sinh \eta \cos \xi H_s' - 4 \cosh \eta \cos \xi H_s'' \\
- 4(\cosh \eta - \cos \xi)^2 H_s + 4 \sinh \eta (\cosh \eta - \cos \xi) H_s' \\
- (\cosh^2 \eta - \cos^2 \xi) H_s'' + 4(\cosh \eta - \cos \xi) \cos \xi (H_s'' - H_s) \\
- 8 \sinh \eta \cos \xi H_s' + 8(1 - \cosh \eta \cos \xi) H_s \\
- (\cosh^2 \eta - \cos^2 \xi) H_s'' + 4 \sinh \eta \cos \xi H_s' \\
\left. - 4 H_s + 4 \cosh \eta \cos \xi H_s + (\cosh^2 \eta - \cos^2 \xi) H_s \right].$$

Adding

$$\delta^2 \nabla^2 \psi_1, \quad \delta^2 \nabla^2 \psi_2 \quad \text{and} \quad \delta^2 \nabla^2 \psi_3$$

and equating to zero the co-efficients of the several powers of  $\cos \xi$ , we obtain the following equations

$$P'' - 9P = 0 \quad \dots \quad (12)$$

$$6 \cosh \eta P + 8 \sinh \eta P' + 2 \cosh \eta P'' + H_2 \cdot \cdot \cdot - 4 H_2 \cdot \cdot \cdot = 0 \quad \dots \quad (13)$$

$$\begin{aligned} (2 \cosh 2\eta + 14)P + 4 \sinh \eta \cosh \eta P' - 8 \cosh \eta \times (16 \cosh \eta P + 8 \sinh \eta P') \\ - 8 \cosh^2 \eta P - \cosh \eta H_2 \cdot \cdot \cdot - 4 \sinh \eta H_2 \cdot \cdot \cdot \cdot 4 \cosh \cdot \cdot \cdot H_2 \cdot \cdot \cdot \\ - H_2 \cdot \cdot \cdot \cdot + 2 H_2 \cdot \cdot \cdot - H_2 \cdot \cdot \cdot = 0 \quad \dots \quad (14) \end{aligned}$$

$$\begin{aligned} 2 \cosh \eta \{ (2 \cosh \eta + 14)P + \cosh^2 \eta P'' \} - 26 \cosh^2 \eta P \\ + \cosh^2 \eta H_2 \cdot \cdot \cdot - 4 \cosh^2 \eta H_2 \cdot \cdot \cdot - 4 \sinh \eta \cosh \eta H_2 \cdot \cdot \cdot \\ + 16 \sinh \eta \cosh \eta H_2 \cdot \cdot \cdot = 0 \quad \dots \quad (15) \end{aligned}$$

$$\begin{aligned} \cosh^2 \eta \{ (2 \cosh 2\eta + 14)P + 4 \sinh \eta \cosh \eta P' + \cosh^2 \eta P'' \} \\ - \cosh^2 \eta P + \cosh^2 \eta H_2 \cdot \cdot \cdot + 8 \cosh \eta H_2 \cdot \cdot \cdot - 8 \sinh \eta H_2 \cdot \cdot \cdot \\ - 4 \cosh^2 \eta H_2 \cdot \cdot \cdot + \cosh^2 \eta H_2 \cdot \cdot \cdot - 4 H_2 \cdot \cdot \cdot - 4 \sinh \eta \cosh \eta H_2 \cdot \cdot \cdot \\ + 2 \cosh^2 \eta H_2 \cdot \cdot \cdot - 3 \cosh^2 \eta H_2 \cdot \cdot \cdot + 4 \sinh \eta \cosh \eta H_2 \cdot \cdot \cdot + 4 H_2 \cdot \cdot \cdot = 0 \quad \dots \quad (16) \end{aligned}$$

solving the equations we get,

$$P = A \cosh 3\eta + B \sinh 3\eta.$$

Therefore

$$H_1 = \frac{1}{3}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta.$$

$$\begin{aligned} H_2 = -\frac{1}{3}(A \cosh 4\eta + B \sinh 4\eta) + E \cosh 2\eta \\ + F \sinh 2\eta + G\eta + H \end{aligned}$$

$$\begin{aligned} H_3 = \frac{1}{33}(A \cosh 5\eta + B \sinh 5\eta) - \frac{1}{33}(A \cosh 3\eta \\ + B \sinh 3\eta) - \frac{1}{3}(E \cosh 3\eta + F \sinh 3\eta) \\ + I \cosh \eta + J \sinh \eta + K\eta \cosh \eta + L\eta \sinh \eta \end{aligned}$$

substituting in the equations (15) and (16) we obtain

$$\left. \begin{array}{l} G=0 \\ K=0 \end{array} \right\} \quad \dots \quad (17)$$

Therefore

$$\begin{aligned} \psi = & \left\{ \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta \right. \\ & + D \sinh \eta \} \sin \xi + \left\{ -\frac{1}{8}(A \cosh 4\eta + B \sinh 4\eta) \right. \\ & + E \cosh 2\eta + F \sinh 2\eta + H \} \frac{\sin \xi}{(\cosh \eta + \cos \xi)} \\ & + \left\{ \frac{1}{8}(A \cosh 5\eta + B \sinh 5\eta - A \cosh 3\eta - B \sinh 3\eta) \right. \\ & - \frac{1}{4}(E \cosh 3\eta + F \sinh 3\eta) + I \cosh \eta + J \sinh \eta \\ & \left. + L\eta \sinh \eta \right\} \frac{\sin \xi}{(\cosh \eta + \cos \xi)^2} \end{aligned}$$

Let the cross-section of the cylinder be denoted by  $\eta = \beta$  and suppose that it is moving with velocity  $U$  parallel to the axis of  $x$ .

The boundary conditions are when  $\eta = \beta$

$$\frac{\partial \psi}{\partial \xi} = -4cU \sinh \beta \left[ \frac{\cos \xi}{(\cosh \beta + \cos \xi)^2} + \frac{2 \sin^2 \xi}{(\cosh \beta + \cos \xi)^3} \right]$$

$$\frac{\partial \psi}{\partial \eta} = -4cU \sin \xi \left[ \frac{\cosh \beta}{(\cosh \beta + \cos \xi)^2} - \frac{2 \sinh^2 \beta}{(\cosh \beta + \cos \xi)^3} \right]$$

because  $u=U$  and  $v=0$  at the boundary.

We then obtain the following equations (C)

$$\frac{1}{8}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta = 0 \quad \dots \quad (18)$$

$$-\frac{1}{8}(A \cosh 4\beta + B \sinh 4\beta) + E \cosh 2\beta + F \sinh 2\beta + H = 0 \quad \dots \quad (19)$$

$$\frac{1}{8}(A \cosh 5\beta + B \sinh 5\beta - A \cosh 3\beta - B \sinh 3\beta)$$

$$- \frac{1}{4}(E \cosh 3\beta + F \sinh 3\beta) + I \cosh \beta + J \sinh \beta$$

$$+ L\beta \sinh \beta = -4cU \sinh \beta \quad \dots \quad (20)$$

$$\frac{1}{3}(A \sinh 3\beta + B \cosh 3\beta) + C \sinh \beta + D \cosh \beta = 0 \quad \dots \quad (21)$$

$$-\frac{1}{3}(A \sinh 4\beta + B \cosh 4\beta) + 2E \sinh 2\beta + 2F \cosh 2\beta = 0 \quad \dots \quad (22)$$

$$\begin{aligned} & \frac{1}{3}(A \sinh 5\beta + B \cosh 5\beta) - \frac{1}{3}(A \sinh 3\beta \\ & + B \cosh 3\beta) - \frac{1}{3}(E \sinh 3\beta + F \cosh 3\beta) \\ & + I \sinh \beta + J \cosh \beta + L(\sinh \beta + \beta \cosh \beta) = -4cU \cosh \beta \end{aligned} \quad (23)$$

At a point near infinity

$$\eta = \delta\eta, \quad \xi = \pi - \delta\xi$$

$$\cosh \eta - \cos \xi = 2$$

$$h = (16c)^{-1} (\delta\eta^2 + \delta\xi^2)^{3/2}$$

In order that  $h \frac{\partial \psi}{\partial \xi}$  may vanish at infinity, the expression

$$\begin{aligned} & \frac{1}{3}\{ (A \cosh 5\eta + B \sinh 5\eta) - (A \cosh 3\eta + B \sinh 3\eta) \} \\ & - \frac{1}{3}(E \cosh 3\eta + F \sinh 3\eta) + I \cosh \eta + J \sinh \eta + L\eta \sinh \eta \end{aligned}$$

must be of the second order of small quantities. This gives the equations

$$\begin{aligned} -\frac{1}{3}E + I &= 0 \\ \frac{1}{16}B - \frac{1}{3}F + J &= 0 \end{aligned} \quad \dots \quad (24)$$

In order that  $h \frac{\partial \psi}{\partial \eta}$  may vanish at infinity, the expression

$$\begin{aligned} & (\cosh \eta + \cos \xi) \{ \frac{1}{3}(A \sinh 5\eta + B \cosh 5\eta) \\ & - \frac{1}{3}(A \sinh 3\eta + B \cosh 3\eta) - \frac{1}{3}(E \sinh 3\eta \\ & + F \cosh 3\eta) + I \sinh \eta + J \cosh \eta + L(\sinh \eta \\ & + \eta \cosh \eta) \} - 2 \sinh \eta \{ \frac{1}{3}(A \cosh 5\eta + B \sinh 5\eta) \\ & - \frac{1}{3}(A \cosh 3\eta + B \sinh 3\eta) - \frac{1}{3}(E \cosh 3\eta \\ & + F \sinh 3\eta) + I \cosh \eta + J \sinh \eta + L\eta \sinh \eta \} \end{aligned}$$

must be of the third order of small quantities.



This gives the additional equations

$$\left. \begin{aligned} -\frac{1}{4}E + I &= 0 \\ \frac{1}{16}B - \frac{1}{4}F + J &= 0 \end{aligned} \right\} \quad \dots \quad (25)$$

which are identical with the equations (24)

At a point near the external focus,

$$\eta = \delta\eta, \quad \xi = \delta\xi$$

$$\cosh \eta + \cos \xi = 2$$

and

$$h = c^{-1} (\delta\eta^2 + \delta\xi^2)^{-1/2}.$$

In order that the velocity may be finite at this point, the expression

$$\begin{aligned} & \left\{ \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \right. \\ & + \frac{1}{4} \left\{ -\frac{1}{8}(A \cosh 4\eta + B \sinh 4\eta) + (E \cosh 2\eta \right. \\ & + F \sinh 2\eta) + H \} + \frac{1}{8} \left\{ \frac{1}{8}(A \cosh 5\eta + B \sinh 5\eta \right. \\ & - A \cosh 3\eta - B \sinh 3\eta) - \frac{1}{4}(E \cosh 3\eta + F \sinh 3\eta) \\ & \left. + I \cosh \eta + J \sinh \eta + L \eta \sinh \eta \right\} \end{aligned}$$

must be of the first order of small quantities.

This gives the equation

$$\frac{1}{16}A + C + \frac{1}{4}E + \frac{1}{4}H = 0 \quad \dots \quad (26)$$

where we have taken into account the equation (24).

We have not yet obtained sufficient number of equations to determine all the un-known constants. In fact we have obtained nine equations, *viz.*, (18), (19), (20), (21), (22), (23), (24) and (26) but there are ten un-known constants in the expression for  $\psi$ . The remaining equation follows from the continuity of motion.

It is easily seen that  $\frac{\partial \psi}{\partial \eta}$  changes sign in passing from one side of the double lines  $\eta=0$  to the other. Hence it is continuous along the line  $\eta=0$ .

But  $\frac{\partial \psi}{\partial \xi}$  does not change sign when we write  $-\xi$  for  $\xi$ . Hence in order that the motion may be continuous,  $\frac{\partial \psi}{\partial \xi}$  must be zero at  $\eta=0$ .

This gives the two additional equations

$$\left. \begin{aligned} \frac{1}{4}A + C &= 0 \\ -\frac{1}{4}A + E + H &= 0 \end{aligned} \right\} \quad \dots \quad (27)$$

From these two equations the equation (26) follows at once.

Thus we get ten equations to determine the ten un-known constants.

Solving, we have

$$A = -8C = 8H = (4cU/S) \sinh 2\beta$$

$$B = (-4cU/S) \cosh 2\beta$$

$$D = (cU/2S)(\cosh 2\beta + 2)$$

$$E = I = 0$$

$$F = (-cU/S)$$

$$J = (cU/4S)(\cosh 2\beta - 6)$$

$$L = (-cU/S) \sinh 2\beta$$

and 
$$S = \frac{1}{4} \{ \beta \sinh 2\beta - (\cosh 2\beta - 1) \}$$

It is easily seen that

$$A + 4L = 0 \quad \dots \quad (28)$$

It may be remarked that the vorticity and velocity-gradients are finite everywhere.

*The Pressure.*

9. Since  $\mu \nabla^2 \psi$  and  $p$  are conjugate functions, we find after a little simplification that

$$p = \frac{\mu}{16c^2} [A \{ -\frac{1}{4} \sinh 3\eta \cos 3\xi - \sinh 2\eta \cos 2\xi \\ - \frac{1}{4} \sinh \eta \cos \xi \} + B \{ -\frac{1}{4} \cosh 3\eta \cos 3\xi \\ - \cosh 2\eta \cos 2\xi - \frac{1}{4} \cosh \eta \cos \xi \} - F \{ 2 \cosh 2\eta \cos 2\xi \\ + 8 \cosh \eta \cos \xi \} - 2L \sinh \eta \cos \xi] + \Pi_0.$$

It is clear that the pressure is finite everywhere.

*The Resistance.*

10. When  $\eta = \beta$ ,

$$\frac{\partial h^*}{\partial \xi} = -\frac{1}{8c^2} \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)^2} (2 \cosh \beta - \cos \xi) \sin \xi$$

$$\frac{\partial h^*}{\partial \eta} = \frac{1}{8c^2} \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)^2} (\cosh \beta - 2 \cos \xi) \sinh \beta$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = -4cU \sinh \beta \left[ -\frac{\sin \xi}{(\cosh \beta + \cos \xi)^2} \right. \\ \left. + \frac{6 \sin \xi \cos \xi}{(\cosh \beta + \cos \xi)^3} + \frac{6 \sin^3 \xi}{(\cosh \beta + \cos \xi)^4} \right]$$

$$\frac{\partial^2 \psi}{\partial \xi \partial \eta} = -4cU \left[ \frac{\cosh \beta \cos \xi}{(\cosh \beta + \cos \xi)^2} + \frac{2 \cosh \beta \sin^2 \xi}{(\cosh \beta + \cos \xi)^3} \right. \\ \left. - \frac{2 \sinh^3 \beta \cos \xi}{(\cosh \beta + \cos \xi)^3} - \frac{6 \sinh^3 \beta \sin^2 \xi}{(\cosh \beta + \cos \xi)^4} \right]$$

$$\frac{\partial^2 \psi}{\partial \eta^2} = \sin \xi \left[ f_1(\beta) + \frac{f_2(\beta)}{(\cosh \beta + \cos \xi)^2} + \frac{f_3(\beta)}{(\cosh \beta + \cos \xi)^2} \right. \\ \left. + 24cU \frac{\sinh \beta \cosh \beta}{(\cosh \beta + \cos \xi)^2} - 24cU \frac{\sinh^2 \beta}{(\cosh \beta + \cos \xi)^2} \right]$$

while  $\frac{\partial \psi}{\partial \xi}$  and  $\frac{\partial \psi}{\partial \eta}$  are given by (C) and

$$f_1(\beta) = \left\{ \frac{1}{2}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta \right\}$$

$$f_2(\beta) = \left\{ -2(A \cosh 4\beta + B \sinh 4\beta) + 4F \sinh 2\beta \right\}$$

$$f_3(\beta) = \left\{ \frac{1}{2}(A \cosh 5\beta + B \sinh 5\beta) - \frac{2}{3}A \cosh 3\beta \right.$$

$$\left. + B \sinh 3\beta \right\} - \frac{2}{3}F \sinh 3\beta + J \sinh \beta$$

$$+ L(2 \cosh \beta + \beta \sinh \beta) \}.$$

Substituting in the expression for the rates of elongation of the shear, we find that

$$e = f = 0$$

$$\gamma = \frac{\sin \xi}{16c^2} \left\{ f_1(\beta) \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)} + f_2(\beta) \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)} \right. \\ \left. + f_3(\beta) \frac{(\cosh \beta + \cos \xi)}{(\cosh \beta - \cos \xi)} \right\} + \frac{U}{4c} \sinh \beta \sin \xi \frac{(\cosh \beta + \cos \xi)}{(\cosh \beta - \cos \xi)}.$$

The resistance is given by

$$R = \int \left( p \frac{dy}{ds} - \mu \gamma \frac{ds}{ds} \right) ds$$

where the integration is taken round the boundary of the elliptic limaçon.

Integrating, we have

$$R = 4\pi\mu U / (\beta - \tan h\beta)$$

My best thanks are due to Dr. N. M. Bose for the interest he has taken in the preparation of the paper.

*Note.*—Although it has been shown that the velocity is everywhere finite and continuous and the rate of change of velocity everywhere finite, yet it is found that the rates of changes of velocity, viz.,  $\frac{\partial^2 \psi}{\partial x^2}$  and  $\frac{\partial^2 \psi}{\partial y^2}$  are discontinuous across the double lines  $\eta=0$ . Therefore the surface traction  $p_{xy}$  is discontinuous across  $\eta=0$ . It is probable that the motion is due to a prescribed velocity across the lines  $\eta=0$ . The phenomenon is a matter for subsequent examination. The detailed examination will follow later on

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# The Scattering of Light by Solid Surfaces

BY

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- (1) Introduction.
- (2) Scattering by Transparent Crystals.
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### (1) *Introduction.*

When a beam of light falls on a transparent body, besides the usual phenomena of reflection, refraction and internal scattering, a small but appreciable fraction of the light is also scattered by the bounding surfaces in all directions. That this phenomenon has been found to be a characteristic property of every solid and liquid surface in our laboratory was announced by Dr. Raman in a preliminary communication to "Nature," August 25, 1923. Since then detailed experimental work concerning the nature of the intensity and polarisation of the scattered light in different directions has been done on the subject with crystalline and amorphous solids, solid metals, liquid mercury, and a large number of liquids. In a paper \* recently communicated to the Royal Society Schuster points out that "the light which enters the optically rarer medium at or beyond the critical angle is an effect of diffraction originating near the boundary of the

\* "Nature," November 22, 1924, p. 772 (see 'note' at the end of the paper).

refracting surface." This is easily seen to be a special case of the phenomenon which forms the subject of this paper. This field of work is extremely interesting as it throws light on the nature and disposition of the molecules at the surface of a body.

In the present paper a detailed description of the experimental results obtained in the case of solid substances is given, the work on liquids forming the subject for a separate paper.

## (2) *Scattering by Transparent Crystals.*

In the ordinary treatment of optical problems on the electromagnetic theory, the reflection of light at a surface is explained as arising from the difference of the properties of the media on the two sides of the boundary. From a molecular point of view, on the other hand, reflection may be regarded as due to the secondary radiation from the electric doublets induced by the infalling waves in the molecules near the boundary forming a regular wave-train which travels back towards the source. The simplest case to consider is that of a transparent crystal bounded by a plane face where the doublets occupy fixed positions in a space lattice and are disposed in a periodic manner on the surface. It is then easily seen that the effect of the secondary radiations in the first medium disappears by interference in all directions except that of the regular reflection from the surface. Theory thus indicates that when light waves fall on the cleavage face of a transparent crystal, we should have only regular reflection and no scattering at the boundary.

A convenient substance for the study of the phenomenon is mica which cleaves easily and gives an ideal surface free from ups and downs larger than a few light waves. Freshly cleaved mica, when placed at the focus of a short-focus lens of large light-gathering power, fails to show any blue opalescence at the surface except some diffraction effects due to dust or

striae. It is very difficult to keep the surface of the mica fresh for any length of time as the dust in the air is caught with wonderful rapidity. The actual difficulty in observing the surface opalescence, if any, is due to the strongly lit-up dusty tracks of the incident, reflected and refracted beams, which appear like a cross, the centre of the cross being the spot on which the light falls on the mica surface. To avoid this trouble two jets of dust-free carbon-di-oxide or air were directed against the spot from either side so as to get clean, dust-free tracks which would not prevent the surface effects from being observed. Even this was insufficient as the background was not very satisfactory. The defect of the background was got over by using a fairly large wooden cross tube provided with suitable apertures and a thoroughly blackened green bottle for the background. Any chinks left were covered up very carefully with black velvet cloth. With this arrangement, when a slow current of dust-free oxygen was maintained through the cross-tube to keep out dust, the polarisation of the oxygen track could be measured with great ease. A freshly cleaved piece of mica was introduced into the centre of the cross-tube through a narrow slot above and light focussed on it. The reflected light was carefully adjusted so as not to interfere with the background in any way. Even under such excellent conditions no sign of any scattering by the surface could be detected. When a piece of coloured mica was tried, however, a feeble blue spot could be seen. It was at first presumed to be the scattering by the surface; but on introducing pieces of increasing thickness the spot was observed to increase in intensity showing thereby that the apparent surface effect is really due to the molecules of the colouring matter inside the mica. An examination of the blue spot with a microscope does not reveal any structure. This experiment confirms the expectation from theory that the irregularities of the surface due to thermal agitation are negligible so far as our present phenomenon is concerned.



Pieces of clear quartz cracked under controlled static compression were next examined with light focussed by a microscope objective which gave a very intense focus. The surface of the conchoidal fracture was so irregular and the most carefully made crack so full of fine quartz dust that the observations failed to reach any definite conclusion. Sometimes by chance, clear portions against a tolerable background could be secured which showed no scattering. It may as well be remarked now that it is impossible to make a given surface sufficiently clean for the observation of surface scattering by any chemical or physical methods. Washing with acids, alkalis and distilled water, etc., however carefully done, leave some kind of dirt or other which show very intense spots when placed at the focus of the beam of light. Starting with a freshly cleaved surface, the influence of these methods of cleaning can be studied. The intensity after chemical cleansing is thousand times greater than what it was before.

Besides quartz, crystals of calcspar, rock-salt, etc., were tried ; but the cleaned surfaces are indeed too poor in quality. On the whole, the above experiments indicate that the surface opalescence in the case of crystals is extremely small.

In the case of a clear block of ice, when light is focussed on the surface, a very intense spot is shown up by the melting surface. If the water formed is blown away by a jet of oxygen or carbon-di-oxide, a feeble blue surface opalescence is visible. By sufficiently increasing the force of the jet of gas, a stage is reached when the intensity of the scattering does not diminish any further. Under the conditions of the experiment it is difficult to say whether the phenomenon is to be ascribed to the surface of ice or to the incipient film of water which the stream of gas may not be able to remove.

### (3) *Scattering by Amorphous Solids.*

Under this heading come the various kinds of glass. We had a very fine collection of the various grades of optical glass

manufactured by Messrs. Schott and Genossen of Jena. Some of these were used in the following experiment.

The specimen to be examined was cracked as before under a screw-press and the fresh surfaces secured examined immediately afterwards. In every case a rather strong and bluish-white opalescence was observed at the surface. When examined by a microscope the focal spot was found to be resolved into very uniformly distributed fine specks just as a fairly thick oil film on water (several molecules thick), when examined in the same way, exhibits microscopic droplets. It is remarkable that the appearance in these two widely different cases is strikingly similar. A description of the distribution of intensity of the scattered light and the nature of its polarisation in different directions is given below.

Let us first take the simple case of unpolarised light normally incident on the surface of glass. The intensity is a maximum in the direction of the normally reflected and the transmitted beams. The intensity rapidly diminishes as the direction of observation is shifted towards the plane of the surface. The spot shows appreciable polarisation in this position when examined with a double-image prism. The stronger component has its electric vector parallel to the surface.

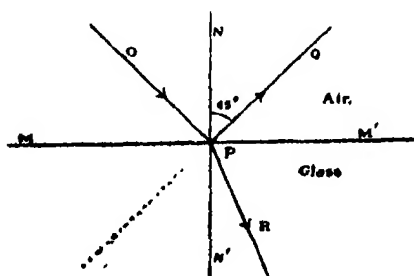


Fig (i)

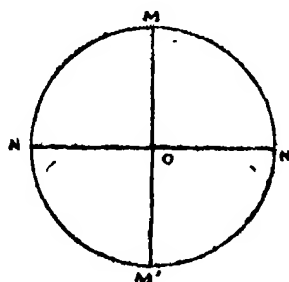


Fig (ii).

When the angle of incidence is  $45^\circ$  and the plane of observation is the plane of incidence (see Fig. i), in directions

near MP, the vertical component, *i.e.*, the one perpendicular to the surface, is slightly stronger. In directions lying between OP and PQ, the component parallel to the surface, *i.e.*, horizontal, is slightly stronger. In a direction near PQ, the reflected ray, the spot is unpolarised. Between PQ and PM the horizontal component increases enormously in brightness until, parallel to M'P, it is completely polarised, the weaker component perpendicular to the surface being exceedingly feeble. On the glass side, in directions lying between PM and PQ' the horizontal component parallel to the surface is slightly stronger and in directions between PR and PM' the vertical component is only slightly stronger even when the direction is almost parallel to PM. In the direction PR the spot is unpolarised.

As regards the distribution of intensity, the intensity is maximum along PQ and PR. On the air side it is a minimum along PM and, excluding directions near PQ, more intense along PM'. On the glass side the intensity in every direction is much more than that on the air side and the intensity is more between PR and PM' than between PN' and PM.

When the plane of observation is confined to the plane at right angles to the plane of incidence, the intensity of scattering is, as before, maximum in the direction of the reflected and transmitted light. The total amount of light scattered in this plane at even small angles with the normal PN is indeed exceedingly small. In Fig (ii) MM' is the surface of glass held vertically and NN' the normal to it. The circle has the opalescent spot O as its centre. MNM' is on the air side and MN'M' on the glass side. In the direction OM the light is partially polarised with its stronger component parallel to the surface of the glass and at right angles to the plane of the paper. This polarisation is a maximum for normal incidence and gets less and less as the angle of incidence increases, while the reverse is true in the

direction  $PM'$  in the plane of incidence (see Fig. *i*). On the glass side also the spot shows polarisation with vibrations parallel to the surface and perpendicular to the plane of the paper in directions near  $OM$ . Along  $ON$  and  $ON'$  it is unpolarised. The above observations bring out the main points of interest with regard to the scattering of light by a surface of glass.

In this connection one observation is noteworthy. In the act of cracking the glass block, some fine glass dust usually clings to some parts of the fresh surfaces and render observations on the air side extremely difficult. All the observations have to be made at some places free from such dust. On the glass side, however, the presence of the dust particles does not at all interfere with the observations. One can always get a clean and fairly intense white spot. This is evidently due to the fact that the particles in question are not in optical contact with the fresh surface of glass (a film of air separates them) and so the light scattered by them into the glass is refracted into a small cone with its axis along the normal to the surface and its half-angle equal to the critical angle for glass. On the other hand the dirt on an old surface or even a grease spot on a fresh surface behaves quite differently, giving as it does a much more intense spot on both sides, the intensity being several hundred times that in the case of the genuine surface effect.

#### (4) *Scattering by Metals.*

The case of metals is essentially different from that of non-conductors like glass. The nature of the polarisation effects in the case of the solid metals and the ideal liquid mercury surface were found to be very similar. The surfaces were polished with great care and were apparently quite good. Microscopic examination, however, revealed irregularities which are very difficult to get rid of. This is evidently due to the extreme softness of the metals. The metals used were

gold, silver, copper, iron, nickel, zinc, aluminium and brass. With all of them similar results were obtained. The following is a brief description of the experimental results.

The characteristic property of the metallic surface is to scatter normally incident, unpolarised light in directions parallel to the surface with the electric vector of the stronger component perpendicular to the surface. The vibration in the incident beam which is mainly responsible for this lies in the direction of observation.

### 1. ALUMINIUM (PLANE OF THE REFLECTING SURFACE VERTICAL).

#### (a) *Normal incidence of unpolarised light.*

Observed parallel to the surface with a double image prism, the component with vibrations perpendicular to the surface is very very intense. On moving towards the normal to the surface, the weaker component continues to be weak.

#### (b) *Normal incidence—light polarised with vibrations vertical.*

In the horizontal plane containing the incident beam, when the spot is viewed parallel to the surface with the double image prism, the two components are almost equal, the slightly stronger component having vibrations parallel to the surface, *i.e.*, vertical. The vertical component increases in intensity as the normal to the surface is approached.

In the vertical plane at right angles to the surface, viewed parallel to the surface, the component with vibration perpendicular to the surface is distinctly brighter and remains brighter as the normal to the surface is approached.

#### (c) *Oblique incidence—light polarised with vibrations vertical.*

Observing from every possible direction in the plane of incidence the stronger component has always its vibrations vertical. In the plane at right angles to the plane of incidence, the stronger component has vibrations perpendicular

to the surface when observed parallel to the surface and on moving towards the normal the same component remains stronger, its vibrations while observing normal to the surface being vertical. In all directions in this plane the scattered light is very strongly or almost completely polarised.

When the incident light is polarised with the electric vector horizontal, for all directions of observation in the plane of incidence the stronger component has always its vibrations horizontal. In the other plane the horizontal vibration is only slightly stronger when observing parallel to the surface and in all directions the contrast between the two components is not very marked.

Lastly, when the incident light is unpolarised and the angle of incidence is nearly  $85^\circ$ , the maximum polarisation in the plane of incidence is away from the reflected light with the strong component horizontal and the minimum polarisation is near the reflected light. In the other plane at right angles to the plane of incidence, the stronger component has vibrations normal to the surface when observing parallel to the surface, the contrast between the two components decreasing as the normal to the surface is reached.

## II. COPPER (PLATE HELD VERTICALLY).

### (a) *Normal incidence of unpolarised light.*

Observing parallel to the surface, the stronger component has vibrations normal to the surface and is coloured red, the ratio  $\frac{\text{red component}}{\text{white component}}$  decreasing as the normal to the surface is approached.

(b) For oblique incidence of unpolarised light in every direction either in or at right angles to the plane of incidence the coloured component, with vibrations normal to the surface when observing parallel to it, is stronger, more so away from the direction of the reflected beam than towards it.

(c) *Light polarised with vibrations vertical.*

For all angles of incidence the coloured component, with vibrations normal to the surface while observing parallel to it, is decidedly weaker when the observations are confined to the plane of incidence. In the plane at right angles to the plane of incidence the stronger component, when the observation is along the surface, has vibrations normal to the surface but is the whiter of the two. The weaker component has a very rich red colour. The ratio of  $\frac{\text{strong component}}{\text{weak component}}$  increases as one approaches the direction of reflection.

When the incident light is polarised with its vibrations horizontal, viewing in the plane of incidence, the stronger component has in all directions its vibrations horizontal and remains stronger for all angles of incidence. In the plane at right angles to the plane of incidence the ratio of the component which is coloured and with vibrations normal to the surface on observing parallel to it to the other component approaches unity as the angle of incidence is slowly increased.

III. Iron, zinc and brass also behave like aluminium and copper. In the case of brass, the coloured and stronger component has vibrations normal to the surface and is yellow, the fainter component being bluish.

A concave galvanometer mirror manufactured by Adam Hilger with a gold on quartz surface was tried and found to give results very similar to those given by the other substances. The polish was very much better and the intensity of the scattered light was on that account very small. On observing the opalescent spot with a microscope, although many specks and spots and other irregularities were very prominent, careful observation revealed a general background illumination which could scarcely be mistaken for any other effect other than genuine surface scattering.

Actual measurements of the nature of the polarisation of the scattered light were taken with the help of a double-image prism and a nicol rotating on a graduated circle in the usual way. We give below the results for two typical cases like iron and copper. It must be pointed out that these measurements are not to be taken as final as they have to be verified for metallic surfaces with perfect polish. The present measurements, however, show the general nature of the phenomenon.

### I. IRON.

$\phi$ —angle of observation with reference to the reflecting surface; for grazing incidence  $\phi=0$  lies on the side away from the reflected light.

$\theta$ —half the difference between the reading of the nicol for the two positions of equality.

$\tan^2 \theta$ —ratio of the weak to the strong component.

#### (a) *Normal Incidence of Polarised Light.*

TABLE I.

$\phi$	$\tan^2 \theta$ for vertical vibrations	$\tan^2 \theta$ for horizontal vibrations.
15°	140	
20°	·112	·008
30°	·082	·011
40°	·050	·017
50°	·031	·015
60°	·020	·011
70°	·013	·011



*(b) Grazing Incidence of Polarised Light.*

TABLE II.

$\phi$ in plane of incidence.	$\tan^2 \theta$ for vertical vibrations.	$\tan^2 \theta$ for horizontal vibrations.
30°	·072	·088
40°	·072	045
50°	082	045
60°	088	058
70°	071	045
80°	·071	·084
90°	·046	081
100°	088	·025
110°	·084	·025
120°	017	·020
180°	·006	015
140°	·005	·009

*(c) Incidence of polarised light at 45°—Observations in the plane at right angles to the plane of incidence.*

TABLE III.

$\phi$	$\tan^2 \theta$ for vertical vibrns.—weak comp. is always horizontal.	$\tan^2 \theta$ for horizontal vibrns. strong comp. is always horizontal.
15°	053	1·000
30°	·088	·428
45°	·187	·270
60°	·160	·189
90°	·180	·188

## II. COPPER (OBSERVATIONS TAKEN WITH RED FILTER).

## (a) Normal Incidence of Polarised Light.

TABLE IV.

$\phi$	$\tan^2 \theta$ for vertical vibrations	$\tan^2 \theta$ for horizontal vibrations.
10°	·528	·081
20°	·490	·088
30°	·361	·041
40°	·288	·049
50°	·198	·049
60°	·147	·039

## (b) Grazing Incidence of Polarised Light.

TABLE V.

$\phi$ in plane of incidence	$\tan^2 \theta$ for vertical vibrations.	$\tan^2 \theta$ for horizontal vibrations.
30°	·336	·125
40°	·250	·129
50°	·230	·123
60°	·211	·112
70°	·185	·106
80°	·130	·088
90°	·130	·069
100°	·064	·045
110°	·067	·034
120°	·036	·031
130°	·030	·030
140° (near reflected ray).	·008	·030

## (c) Incidence of polarised light at 45°—Observations in the plane at right angles to the plane of incidence.

TABLE VI.

$\phi$	$\tan^2 \theta$ for vertical vibrns. weak comp. is always horizontal.	$\tan^2 \theta$ for horizontal vibrns strong comp. is always horizontal.
15°	·100	·391
30°	·100	·307
45°	·100	·240
60°	·060	·171
90°	·073	·040

(5). *Summary and Conclusion.*

(1) The scattering of light by freshly cleaved surfaces of mica, quartz and other crystals has been found experimentally to be negligible and this is quite in agreement with theory.

(2) The opalescent spot shown up by a freshly cracked surface of an amorphous substance like glass has an intensity much smaller than the intensity in the case of a chemically cleaned surface of the same substance. When examined with a microscope, the spot is resolved into uniformly distributed fine specks very similar in appearance to those seen on an oil film on water when examined in the same way. The nature of the polarisation and the distribution of intensity of the scattered light in different directions has been described.

(3) The scattering by polished metallic surfaces is essentially different from that by a non-metallic surface. The main features of the polarisation effects are described for various metals and the measurements of the polarisation in different directions in the case of iron and copper are given.

The author intends following up the experimental work in connection with metallic surfaces obtained by means of cathode sputtering. The surfaces of thick films of metal obtainable by this method would be much better than those prepared by ordinary polishing and may lead to more reliable and accurate data than those obtained hitherto.

In conclusion, the author wishes to express his best thanks to Prof. C. V. Raman for his valuable help and encouragement.

*Note.*

While this paper has been in the press, Schuster's paper referred to on page 129 has appeared (Proc. Roy. Soc. Vol. 107, January 1925). Schuster's point of view is now seen to be quite different from that of the

present paper. He has not dealt with the fundamental problem of surface scattering, an effect due to the inherent thermal fluctuations of the surface, but has treated the problem of diffraction of light in the ordinary way arising from the finite width of the incident beam or the finite length of the surface illuminated. In the latter case no special properties of the surface of separation are directly concerned. The effect is wholly due to the geometry of the incident beam and "the ratio of the total energy dissipated into space by diffraction to the total energy of the incident light is inversely proportional to the square root of the length of the refracting surface and therefore tends towards zero as the size of the refracting surface increases." According to Schuster's calculations, the effect in his case is of a much higher order of magnitude than that of surface scattering as may be expected. A more complete discussion is reserved for a later paper.

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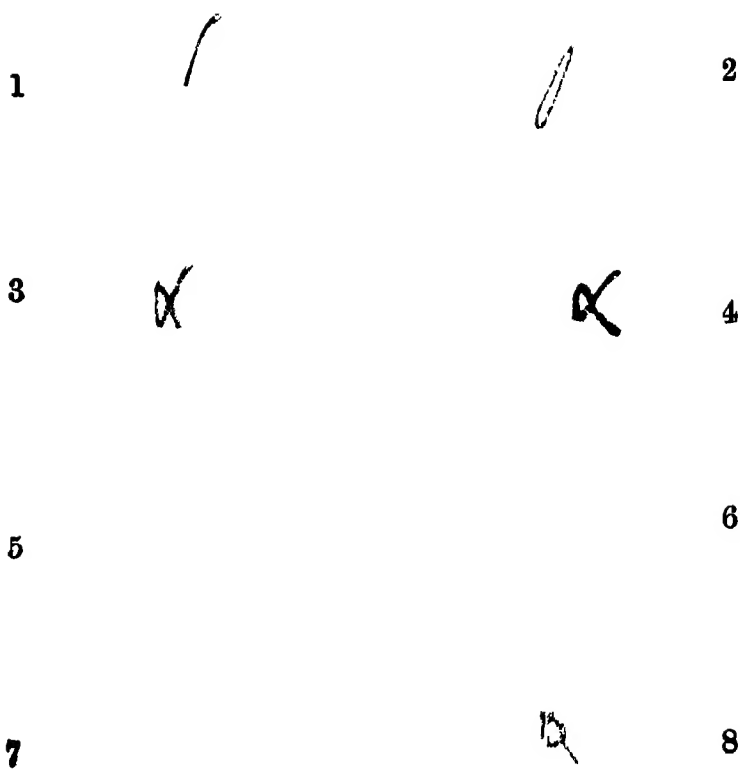


PLATE II.

# Forced Vibrations of Finite Amplitude of Stretched Strings.

By

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## *Synopsis.*

[The paper contains a description of the experiments with the longitudinal mode of Melde's experiment in which the ratios between the period of the vibrator and the string are  $2/2$ ,  $3/2$ ,  $4/2$ ,  $5/2$ , etc. It has been found that in all these cases (1) the phase difference between the vibrator and the string alters with the changes of tension in a particular manner for a given ratio, and (2) that the amplitude of the maintained motion is small when the tension is high, increasing with the diminution of tension and reaching a limiting value at a certain low tension beyond which the motion collapses suddenly.

Raman's theory has been slightly extended and the formulæ modified by taking into consideration the finite amplitude of motion and adding a term  $\beta y^2$  to  $n^2$  in the equation of motion. Separate formulæ have been given for the ratios  $2/2$ ,  $3/2$  and  $4/2$ . They show agreement with (1) and (2) and further indicate that the amplitude is determinate.]

In a recent paper<sup>1</sup> the author has shown that, when the amplitude of motion of a stretched string one metre long is about 3 or 4 cms, the damping is proportional to the second power of the velocity. When, however, the amplitude is not so large, the damping is proportional to the first power of the velocity. In the course of some experimental work with the forced vibration of stretched strings under different types of excitation, results have been obtained which show that the finite amplitude of motion must be taken into consideration.



The present paper describes experiments with the longitudinal mode of Melde's experiment in which the ratio between the period of the vibrator and the string is  $m/2$  where  $m$  is an integer, and compares them with the theory of the longitudinal mode of forced vibration of finite amplitude that has been developed here. These experiments were performed with a motor vibrator. To the shaft of a motor a disk carrying a slotted plane is fixed, and a crank pin is screwed to a piece sliding on the slot. The crank pin is again connected to a rocking lever. When the motor revolves, the lever (vibrator) performs a simple harmonic motion and can replace the tuning fork in Melde's experiments. One very great advantage of the Motor vibrator is that the magnitude of oscillation of the vibrator remains constant for different tensions. Ordinary twisted cotton thread was tied to a hook of the vibrator and the tension was adjusted by weights. The plane of motion of the vibrator was parallel to the string. The phase relation between the vibrator and the string was studied by attaching a bright lead to the string near the vibrator, and observing the Lissajous' figure at various stages of the tension and amplitude. (A fuller description of the method of experimentation and of the Motor vibrator is given in the Proceedings of the Indian Association for the Cultivation of Science, Vol. VI, Parts I and II, and Physical Review, November, 1919.) In the longitudinal mode of excitation, Prof. Raman has shown<sup>1</sup> that maintenance is possible when the ratio between the period of the vibrator and the string is  $m/2$ ,  $m$  being an integer. For the first type  $m=1$ , the experiments performed with the help of the Motor vibrator have been fully described.<sup>2</sup> The cases studied here are those for which the ratios are  $2/2$ ,  $3/2$ ,  $4/2$ ,  $5/2$ . It has been found that for all the higher types, the magnitude of the obligatory motion must be large, and the length of the string should be small.

<sup>1</sup> Physical Review, December, 1912

<sup>2</sup> Proc. Ind. Assn., Vol. VI, Parts I and II.

In all the cases described in this paper, the amplitude of the vibrator and the length of the string were kept the same. The motion for a given type is started with a large tension, and as the tension is gradually diminished, the amplitude of motion of the string continuously increases, and the phase difference alters, till a limiting value of the amplitude is reached beyond which a slight decrease in tension causes a sudden collapse of the maintenance. This differs from the ordinary case of resonance where the amplitude becomes maximum when the natural period of oscillation of the system equals that of the force.

With the increase of the amplitude of the vibrator, the motion of the string for a given type and the range of resonance increase; but, for the same amplitude of the vibrator, the resulting motion and the range of resonance go on decreasing with increasing values of  $m$ .

$m = 2$ .

Figs. (1) and (2) show the Lissajous' figures in the case when the period of the vibrator and that of the string are equal, the former under high tension and small amplitude of motion of the string, and the latter under low tension and small amplitude. It is evident that the phase difference is 0 in (1) and  $\pi/4$  in (2). In this case the curvatures of the boundaries of the oscillating string on the two sides are different.

$m = 3$

Figs. (3), (4) and (5) show the same when the string makes three swings for every two oscillations of the vibrator. From them it will be found that there are two intermediate resting places. The inner ones are the amplitudes at the phases of maximum tension, and the two outer ones correspond to those at the phases of minimum tension. Figs (4) and (5) show the curve under high tension and small amplitude, the phase difference being about  $\pi/4$ . In Fig. (5) it is about zero when the tension is low and the amplitude is large.

$m=4$

In this case, Figs. (6) and (7) show the curve under high tension and low amplitude, and low tension and big amplitude; the phase change is very slight. The maintenance is vigorous and more stable than in the cases  $m=3, 5$ , etc.

$m=5$

Fig. (8) shows the curve in this case. This type is very unstable and requires careful adjustment of the tension. It will be observed that with the increasing value of  $m$ , the phase change and the increase of amplitude go on decreasing.

### *Theory.*

For the first type  $m=1$ , the author has shown<sup>1</sup> that, to account for the changes of phase and the nature of resonance, the damping due to the second power of the velocity must be considered when the amplitude of the motion of the string is large. When the amplitude is small, it is found that the damping is proportional to the first power of the velocity; the phase does not change and it remains almost  $\frac{\pi}{4}$  throughout the range of resonance. For  $m=2, 3, 4$ , etc., Prof. Raman<sup>2</sup> has extended the late Lord Rayleigh's theory<sup>3</sup> with the first power law of damping, but it is not sufficient to account for all the observed facts. For these types, the amplitudes, though not so large as in the case  $m=1$ , are finite and must be taken into consideration in obtaining the value of the restoring force. With this slight modification, the formulæ that are obtained here are found to explain all the observed facts. Assuming that each element of the string moves as if it possesses only one degree of freedom, the equation of motion under a variable spring of period  $\frac{\pi}{p}$  can be written as

$$\ddot{y} + \lambda y + (\alpha^2 - 2\alpha \sin 2pt + \beta y^2)y = 0 \quad \dots (1)$$

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Theory of Sound*, Vol. I, Art. 184.

where the constants have their usual meanings.<sup>1</sup> A term  $\beta y^2$  has been added to  $n^2$  to represent forces for the finite displacement.

$$m = 2.$$

Assume

$$y = Q + A_1 \sin 2pt + B_1 \cos 2pt + A_2 \sin 4pt + B_2 \cos 4pt \quad (2)$$

Substituting (2) in (1) and equating the co-efficient of  $\sin 2pt$ ,  $\cos 2pt$ , etc., we obtain the following relations, neglecting terms  $4pt$ , etc.,

$$Q = \frac{\alpha F_1 \cos E_1}{n^2 + \frac{1}{2}\beta F_1^2} \quad (3)$$

where  $F_1$  is the amplitude and  $E_1$  the phase angle of the  $2pt$  component.

$$\tan E_1 = \frac{2kp}{4p^2 - (n^2 + \frac{1}{2}\beta F_1^2)} \quad (4)$$

$$\Delta^2 = \frac{4\alpha^2 \cos^2 E_1}{n^4} - 4k^2 p^2 \quad \dots (5)$$

where

$$\Delta = n^2 - 4p^2 + \frac{1}{2}\beta F_1^2$$

Equation (3) shows that a constant term in the displacement is necessary. Its magnitude depends upon the amplitude of motion of the string and the phase angle. It can be easily shown that the effect of this term is to produce a difference in the curvature of the vibrating string at the two resting places, due to the fact that the displacements and hence the restoring forces are different on the two sides of the equilibrium position.

<sup>1</sup> Barton's Text-book on Sound, Art. 248.

From (5) we see that maintenance is not possible when  $n$  is very large, but only when

$$a^2 \frac{\cos E_1}{n^2} > kp$$

When  $n > 2p$  by a finite but small quantity, equation (4) shows that  $E_2$  is nearly equal to 0, since  $k$  is small. When  $k$  is nearly equal to  $2p$ ,  $E_2$  comes out nearly equal to  $-\frac{\pi}{4}$  and when  $n < 2p$ ,  $E_2 > -\frac{\pi}{4}$  and approaches the value  $\frac{\pi}{2}$  but cannot reach it since the motion subsides at once as is evident from (5). The effect of the finite amplitude is to render the changes of phase gradual.

When  $n$  is known, the approximate value of  $E_2$  can be calculated from (4) provided  $n \neq 2p$ , and, substituting its value in (5),  $F_2$  can be determined.

When

$$n > 2p, \quad E_2 = 0$$

$$\frac{1}{2} \beta F_2^2 = \left( \frac{4a^2}{n^2} - 4k^2 p^2 \right)^{\frac{1}{2}} - (n^2 - 4p^2) \quad \dots (6)$$

When

$$n = 2p, \quad E_2 = -\frac{\pi}{4},$$

Then

$$\frac{1}{2} \beta F_2^2 = \left( \frac{4a^2}{2n^2} - 4k^2 p^2 \right)^{\frac{1}{2}} \quad \dots (7)$$

and when

$$n < 2p$$

$$\frac{1}{2} \beta F_2^2 = \left( \frac{4a^2}{n^2} \cos^2 E_2 - 4k^2 p^2 \right)^{\frac{1}{2}} + (4p^2 - n^2) \quad \dots (8)$$

where

$$\cos^2 E_2 < \frac{1}{4},$$

so that we observe that the amplitude goes on increasing as  $n$  diminishes from  $n > 2p$  to  $n < 2p$ . It has also been mentioned that the amplitude cannot increase indefinitely with the decrease of  $n$  but reaches its maximum value when  $E_2$  is nearly equal to  $\frac{\pi}{2}$  after which the motion subsides. The limiting value of  $F_2$  can be calculated from

$$4p^2 - n^2 - \frac{1}{4}\beta F_2^2 = 0 \quad (9)$$

We fall back upon Raman's theory by putting  $\beta = 0$ ; then we find that the amplitude  $F_2$  becomes indeterminate, the range of resonance becomes smaller, and the changes of phase expressed by his formulæ become more rapid than is actually the case.

When the tension is large  $n > 2p$  and the phase difference is 0 as shown by the curve (1) and theory. The amplitude is also small as demanded by the theory. When the tension is low  $n < 2p$ , the phase changes to  $-\frac{\pi}{4}$  and the amplitude increases. The sudden collapse of the motion has also been explained.

$m = 3$

The equation of motion is the same as before and we assume

$$y = A_1 \sin pt + B_1 \cos pt + A_3 \sin 3pt + B_3 \cos 3pt + \dots$$

Proceeding in the same way as before, we obtain

$$F_3^2 / F_1^2 = \alpha^2 / \Delta^2 + 9k^2 p^2 \quad (10)$$

where

$$\Delta = n^2 - 9p^2 + \frac{1}{4}\beta F_1^2$$

$$\tan E_3 = \frac{\Delta - 3kp \tan E_1}{\Delta \tan E_1 + 3kp} \quad (11)$$

$$\Delta^2 = a^2 F_1^2 / F_3^2 - 9k^2 p^2 \quad (12)$$

$$\left. \begin{aligned} \tan E_1 &= \left( \frac{a - kp}{a + kp} \right)^{\frac{1}{2}} \\ (n^2 - p^2 + \frac{1}{4}\beta F_1^2) &= a^2 - k^2 p^2 \end{aligned} \right\} \quad (13)$$

In order that  $F_3$  may be large in comparison with  $F_1$ , it is evident from (10) that  $a$  must be large and  $\Delta$  and  $kp$  should be small; and  $\Delta$  is small when  $n$  is nearly equal to  $3p$ . When this is the case equations (13) are simplified to

$$\left. \begin{aligned} \tan E_1 &= 1, \quad E_1 = \frac{\pi}{4} \\ \frac{1}{4}\beta F_1^2 &= (a^2 - 8p^2)^{\frac{1}{2}} \end{aligned} \right\} \quad (14)$$

and

$$\tan E_3 = \frac{\Delta - 3kp}{\Delta + 3kp} \quad (15)$$

We find that when the amplitude of the  $pt$  component is small, its phase angle is about  $\frac{\pi}{4}$  and the amplitude remains constant throughout the range of resonance of the  $3pt$  component.

When  $n > 3p$ ,  $E_3$  comes out to be  $\frac{\pi}{4}$ , and as  $n$  diminishes and reaches the value  $3p$ ,  $E_3$  diminishes and attains the value zero. When  $n < 3p$ ,  $E_3$  is equal to  $-\frac{\pi}{4}$ .

When  $F_1$  is determined from (14),  $F_3$  can be obtained from (12). From (12) it is clear that as  $n$  decreases from  $n > 3p$  to  $n < 3p$  the amplitude of maintained motion increases continuously, but there is a limit beyond which the motion subsides; this happens when the right side of (12) becomes zero. When  $n = 3p$  the magnitude of  $F_3^2$  can be determined from the cubic in  $F_3^2$ ,

$$\frac{9}{16} \beta^2 (F_3^2)^3 + 9k^2 p^2 F_3^2 - a^2 F_1 = 0$$

The maximum value of  $F_1$  is given by

$$F_1 = \frac{2a}{3kp} \left( \frac{a^2 - 8p^2}{\sqrt{3}\beta} \right)^{\frac{1}{2}}$$

Further, it will be observed that the maintenance of the  $3pt$  component is due to the presence of the  $pt$  component.

If we put  $\beta = 0$ , we find that the amplitude should be maximum when  $n = 3p$  which is not the case, and the sudden collapse of the maintenance at a certain value of tension  $n < 3p$  remains unexplained. The change of phase is partly shown by the formulæ.

By comparing the above observations with the experimental facts it will be found that they show good agreement. Figs. (3), (4) and (5) show the change of phase from  $\frac{\pi}{4}$  to zero when the tension diminishes from  $n > 3p$  to  $n$  nearly equal to  $3p$ . Further, the increase of the amplitude and the collapse with diminution of tension have been explained. The tension is above its normal value twice and below normal once in one complete oscillation of the string. This can be easily shown by integrating

$$2a \sin 2pt \quad y \quad \text{over } \frac{1}{4}, \frac{2}{4}, \frac{3}{4}$$

periods respectively. To each of these epochs there corresponds one resting place [see Figs. (3), (4) and (5)]

$$m = 4$$

Assuming

$$y = B_0 + A_1 \sin 2pt + B_1 \cos 2pt + A_2 \sin 4pt + B_2 \cos 4pt,$$

we obtain the following relations on substitution in (1)

$$B_0 = -\frac{4}{3} \frac{a^2 F_1 \sin E_1}{n^2 \{n^2 + \frac{1}{2}\beta(F_1^2 + F_2^2)\}} \quad (16)$$

$$(n^2 - 16p^2 + \frac{1}{2}\beta F_1^2)^2 = a^2 F_1^2 / F_2^2 - 16k^2 p^2 \quad (17)$$

$$4kpF_1 = -aF_1 \cos(E_1 - E_2) \quad \dots \quad (18)$$



When  $B_0$  is small and  $F_4$  is finite,  $E_4$  is nearly equal to zero. The changes of phase with variation of tension and amplitude are shown by (17) and (18). Equation (17) shows that the amplitude cannot go on increasing indefinitely with decrease of tension, but reaches a limit when the right side of (17) becomes zero. The amplitude  $F_4$  is determinate since  $F_2$  is given by (5). Equation (18) expresses the relation between the energy supplied by the variable spring and that lost by friction in any number of complete periods. Since  $E_2$  changes with the variation of tension,  $E_4$  must also change. The maintenance of the  $4pt$  component is due to the presence of the  $2pt$  component. There is one intermediate resting place corresponding to the phase of maximum tension.

We obtain Raman's equations by putting  $\beta=0$ . Then we find as before that the amplitude becomes indeterminate since  $F_2$  becomes indeterminate and according to (17) [ $\beta=0$ ],  $F_4/F_2$  should be maximum when  $n=4p$ ; but this is not the case. The collapse of the motion at a tension  $n<4p$  cannot be explained. The changes of the phase are partly explained by (16).

For other types of excitation, the theory is easily developed in the same way and the sequence of events is found to be the same as described in this paper.

It will be observed that the collapse of the maintenance takes place when

$$\frac{\alpha^2 F_1^2}{F_2^2} - m^2 h^2 p^2$$

becomes zero. Hence as  $m$  increases the range of resonance diminishes for a given value of  $\alpha$ .

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# Surface Tension of Water, Benzene, Methyl and Ethyl Alcohols.

BY

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The object of this investigation is to describe a modification of the ordinary method of measuring surface tension by observing the rise of a liquid in a capillary tube. The modification consists in measuring, by means of a sensitive manometer, the pressure which must be applied to the surface of the meniscus in order to depress it to the level of the free surface of the liquid outside. In practice it was found more convenient to depress the meniscus to a point on the capillary, the depth of which below the free surface of the liquid was accurately known. If  $P$  is the total pressure in centimetres of water required to depress the meniscus  $h$  centimetres below the free surface of the liquid (density  $d$ ), then the capillary rise expressed in centimetres of water of unit density  $= (P - hd) + \frac{1}{8}rd$ ,<sup>1</sup> where  $\frac{1}{8}rd$  denotes the usual correction to be applied to the observed rise for the weight of the liquid in the meniscus.

<sup>1</sup> The correction  $\frac{1}{8}$  to the observed rise is based upon the assumption that the meniscus in the capillary tube is hemispherical. Fergusson (Phil Mag, p 131, 1914), has shown that this assumption approximates to truth, if  $r$  is small in comparison with  $h$  (the capillary rise) and the ratio of  $r$  to  $a$  (where  $a = \frac{T}{gd}$ ) is such that any powers of  $\frac{r}{a}$  higher

than two are negligible in comparison with unity. In this experiment the radius of the tube was about 0.5 mm. and both these conditions are fairly satisfied. L. W. Winkler (Z. Angew. Chem. 1903, p 719) and later T. W. Richard and L. B. Coombs (Jour. Amer. Chem. Soc., p 1666, 1915) have tried to solve this question practically and have shown that this assumption is fairly justified for values of  $r$  as much as 1 mm.

Surface tension is then given by the formula :—

$$T = \frac{1}{2}gr\{(P-hd) + \frac{1}{2}rd\} \quad \dots (A)$$

where  $r$ , as usual, stands for the radius of the capillary tube.

A diagram of apparatus for observing  $P$  and  $h$  is given in Fig. 4. The method will be described under the following heads :—

#### I. Manometer

- (a) Calibration of the U tube
- (b) „ „ „ reservoir.

#### II. Calibration of the capillary tube.

#### III. Preparation and purity of materials.

#### IV. Regulation of temperature.

#### V. Manipulation of the method.

- (a) Arrangement of apparatus.
- (b) Adjustments, method of observation and results
- (c) Advantages of the method.

#### *I. The Manometer*

This manometer (fig. 1 at the end of the paper) is described in *Zeit Analchemie* Vol. 40, page 403 (1901), and it is claimed there, that it is capable of detecting differences of pressure amounting to  $\cdot 00003$  mm. of mercury. It consists of a U tube of uniform cross-sectional area provided with two wider tubes or reservoirs A and B, the cross-sectional areas of which are uniform and  $m$  times that of the U tube. The lower half of the U tube was filled with chemically pure aniline supplied by E. Plomer & Co. of Lahore, and the upper half and a portion of the reservoirs with specially distilled water. On the top of water in each reservoir, is a thin layer of oil to prevent evaporation. Aniline was chosen because it is immiscible with water. The U tube with the reservoirs is fixed to a wooden support provided with levelling screws. Along-side each limb of the U tube is fixed a metre scale, so as to be in the field of view of a comparator simultaneously with the interfacial

meniscus. The position of this interfacial meniscus is noted on the scale by means of a comparator provided with a micrometer reading to  $\frac{1}{1000}$  of a mm.

### *Theory of Manometer.*

CD and AB<sup>1</sup> are oil layers to prevent evaporation; E and G are the menisci of aniline-water surfaces.

Let us consider the simple case, when the axes of the reservoirs and the limbs of the U tube are vertical, the reservoirs are of equal cross-sectional areas and the U tube is of uniform bore. Consider the equilibrium at the point G.

Suppose  $S_o$  stands for the density of oil

$S_w$     „        „        „    water

$S_a$     „        „        „    Aniline, & other letters

have the meaning shown in the diagram. For equilibrium at the point G,

$$hS_o + (p+q)S_w = h'S_o + q'S_w + pS_a \quad \dots (i)$$

Suppose a pressure of X cms. of water of density S is applied to the reservoir A; the meniscus in A will move down through a distance  $z$  and that in B will rise through an equal distance.

$$\therefore hS_o + (p+q+mz-z)S_w + zS = h'S_o + (q'-mz+z)S_w + 2mzS_a \quad \dots (ii)$$

Subtract (i) from (ii)

$$(m'-z)S_w + zS = (-mz)S_w + 2mzS_a$$

<sup>1</sup> The oil layers AB and CD were dispensed with, as they rendered the walls of the reservoirs greasy, causing drops of water to remain sticking behind as the liquid surface rose or fell in the reservoirs. This seriously affected the accuracy of the manometric readings. Their elimination does not affect in any way the reasoning employed in deducing equation III. The mouth of the reservoir CD was closed with a rubber cork through which passed a narrow glass tube provided with a stop cock to put the reservoir in communication with the atmosphere when required. With this arrangement the effects of evaporation were quite inappreciable.

But  $2\,mz$  = change in the difference of level between the two meniscuses E and G. Denote it by  $Q$ ,

$$\therefore \rho S (= P \text{ Say}) = Q \left( S_a - \frac{m-1}{m} S_r \right) \quad (m)$$

The assumptions made in deducing this formula are :—

(a) The axes of the limbs of the U tube and the reservoirs are vertical,

(b) The reservoirs and the U tube are of uniform cross-sectional areas, and

(c) The liquids used (*i.e.*, aniline and water) in the manometer are immiscible.

As regards the first assumption, the limbs of the U tube were bent accurately parallel and made to lie in the same plane. This was tested by mounting the U tube on its stand, and setting one of its limbs vertical by means of a plumb-line. A plumb-line was then hung alongside the other limb, and the two were observed to be parallel. The reservoirs were fixed to the U tube by means of rubber bungs, and their axes were adjusted vertical and parallel in two mutually perpendicular planes by hanging two plumb-lines along-side each.

Non-uniformity of the cross-sectional areas of the reservoirs or the U tube will affect the value of  $Q$  in the above formula, and this effect was allowed for by calibrating both the U tube and the reservoirs.

As regards the third assumption, the solubility of aniline in water or vice versa is very small, both being about 5%. W. Alexejeff in *Berichte der Deutschen Chemischen Gesellschaft*, Vol. 10. p. 709, gives 4.6 parts as the solubility of water in 100 parts of the solution at 8°C. The solubility at 15°C = 5 approx. (Watt's Dictionary of Chemistry). To allow for this, aniline saturated with water was used in the

manometer. Hence in formula III above,  $S_a$  should be taken as the density of aniline saturated with water at the temperature of the experiment. R. J. Friswell's value of the density of aniline saturated with water at  $15^{\circ}\text{C}$  referred to water at  $15^{\circ}\text{C}=1.025$  (Watt's Dictionary of Chemistry). This, when referred to water at  $4^{\circ}\text{C}$ , reduces to  $1.0241$ . Density of pure aniline at the same temperature and referred to water at  $4^{\circ}\text{C}=1.0233$  (R. J. Friswell). Thorp (Jour. Chem. Soc., London, Vol. 37, p. 221) gives  $1.0379$  as the density of aniline at  $0^{\circ}\text{C}$ . From this the density at  $15^{\circ}$  using  $.00085$  (Kaye and Laby's tables) as the co-efficient of cubical expansion of aniline works out to be  $1.024$ . This shows that there is a little contraction in volume on solution, and that its effect is not very marked on density.

The mean of the three concordant values of the density of aniline saturated with water at about the mean temperature of the experiment ( $29.5^{\circ}\text{C}$ ) as determined by the water by the pycnometer method, was found to be  $1.0126$ .

The density of water over the interfacial meniscuses will also be affected by the solution of aniline in it. As the solution proceeds by diffusion, this effect will not rise very far up in the course of a few days, and the reservoirs will probably remain quite unaffected; and it is water entering or leaving a reservoir that really comes into the calculations. So long as the effect remains confined to a few cms. above the inter-facial meniscuses in either limb of the U tube, a little consideration will show, that it will cancel out from equations i and ii. Even at its maximum, the effect is small. Thus the density of water saturated with aniline at  $21^{\circ}\text{C}=.99901$  (Watt's Dictionary of Chemistry); and the density of pure water at the same temperature is  $.99801$  or a difference of about  $.1\%$ . Hence  $S$  in equation III was taken as the density of pure water at the temperature of the experiment without introducing any appreciable error into the calculations.

### *Calibration of the Manometer.*

#### *(a) Calibration of the U tube.*

As will be described later, the U tube was made by sealing together two burettes of very nearly the same cross-sectional areas. Each of the tubes was calibrated by the following method before sealing them together into a U tube.

Suppose the mass of mercury necessary to fill nearly the whole of the graduated portion of the tube is  $M$  gms. Let its length be  $L$  cms. Therefore the average mass of mercury required to fill one centimetre of the tube  $= M/L$  gms. Let  $m_1$  gms. of mercury fill  $a_1$  cms. of the tube between the zero and the  $\perp_1$  th centimetre division. If the tube were of uniform bore, it ought to have occupied a length  $d_1 = \frac{m_1 L}{M}$  cms.,  $(d_1 - a_1) = f_1$  denotes the correction which is to be applied to the tube at  $L_1$  th division. Again let  $m_2$  gms. of mercury fill  $a_2$  cms. of the tube between the  $\perp_1$  th and  $\perp_2$  th cm. division. As before, its length ought to have been equal to  $d_2 = \frac{m_2 L}{M}$  cms. and  $(d_2 - a_2) = f_2$  denotes the correction to be applied to the observed length  $a_2$ ; and hence the total correction to be applied to the  $\perp_2$  th division  $= f_1 + f_2 = c_2$  (say)

Let  $\perp_1, \perp_2, \dots, \perp_{10}; a_1, a_2, a_3, \dots, a_{10}; d_1, d_2, d_3, \dots, d_{10}; f_1, f_2, f_3, \dots, f_{10}; c_1, c_2, c_3, \dots, c_{10}$ .

have similar meanings at different points on the tube;

Since,

$$d_1 - a_1 = f_1, \quad \therefore \quad \text{correction at } \perp_1 = f_1 = C_1$$

$$d_2 - a_2 = f_2, \quad \therefore \quad \text{,,} \quad \perp_2 = f_1 + f_2 = C_2$$

$$d_3 - a_3 = f_3, \quad \therefore \quad \text{,,} \quad \perp_3 = f_1 + f_2 + f_3 = C_3$$

$$\dots \quad \quad \quad \dots \quad \quad \quad \dots$$

$$d_{10} - a_{10} = f_{10} \quad \therefore \quad \text{,,} \quad \perp_{10} = f_1 + f_2 + \dots + f_{10} = C_{10}$$

*Experimental*

After examining a large number of tubes, two tubes were selected from old burettes whose mean cross-sectional areas were very nearly the same—the difference was less than 1 part in 600. One of the tubes after having been carefully cleaned and dried was fixed up vertically alongside a metric scale. Mercury was sucked up into it by means of an air pump, which method proved very successful in getting rid of air bubbles from the walls of the tube. The level of mercury in the tube was adjusted until it stood very near the zero mark on the burette. Mercury was then run into a weighed dry and clean bottle by gently opening the stop cock until the level fell down by about 5 cm. This length (*i.e.*,  $a_1$ ,  $a_2$ ,  $a_3$  ...  $a_{10}$  referred to above) was accurately determined by means of a comparator provided with a micrometer screw graduated to  $\frac{1}{100}$  of a millimetre. Three readings were taken at each end of the mercury column—one reading on the top of the mercury column and the other two on the divisions of the scale between which the meniscus stood. The tube was gently tapped near the meniscus before taking a reading to enable the meniscus to recover its natural form.

Since each measurement of length ( $a_1$ ,  $a_2$ ,  $a_3$ , etc.) is subject to a possible observational error, the corrections will be affected by these errors, and the magnitude of the error at any point at which the correction has been determined will depend upon the number of times the length of the thread has been measured between the extreme points, *i.e.*, upon the number of places along the tube at which the correction has been determined. Consequently two independent sets of observations consisting of about 10 readings each were taken with each tube to diminish the accumulation of these observational errors. The second set of readings lay approximately intermediate in position between those of the first set. The calibration was carried out in an underground chamber, the temperature of which remained fairly constant; the effect



of any slight variations of temperature on lengths  $a_1, a_2, \dots a_{10}$  was calculated and allowed for.

Mean length per unit mass of the tube (A) =  $\cdot 08786$  cms.

„ „ „ „ (B) =  $\cdot 08778$  „

Average length per unit mass for both the tubes  $\cdot 08782$  cms.; therefore the mean cross-sectional area of the U tube at

$$(20^\circ\text{C}) = \frac{1}{\cdot 08782} \times \frac{1}{13 \frac{546}{1000}} \text{ sq cms} = 8409 \text{ sq cms}$$

$\therefore$  mean radius of the U tube =  $\cdot 5174$  cms.

(b) *Calibration of the reservoirs.*

After examining a number of tubes, one was selected about 24 cms. long and with a fairly uniform diameter of about 4 cms. The variations in diameter were less than one part in 100. One end of the tube was closed with a tightly fitting rubber cork. It was held in a retort stand supported on a tripod provided with levelling screws, and it was set vertical in two mutually perpendicular planes by means of two plumb lines hung alongside it. Some water was poured into the tube so as to fill about one or two centimetres of it. An L shaped piece of stout iron wire (see fig. 2) firmly fixed to the carriage of a microscope and carefully levelled so that its pillar was vertical, was lowered into the glass tube until the lower point of the wire was a little below the surface of water. The wire was then raised by rotating the micrometer head attached to the instrument until the point just touched the water surface near its centre. This adjustment could be made with a high degree of accuracy by observing when the point come in contact with its own image formed by reflexion at the water surface. If by accident the point was raised too far up, it was lowered down and then raised again to avoid the error due to the back-lash of the screw head, as the point was subsequently to be raised further to make contact at the higher level. Each setting was repeated

several times and figures concordant to 3 decimal places were always obtained. Distilled water was then poured into the tube from a wash bottle until the level of water rose to within a centimetre or two of its upper end. The wash bottle was afterwards weighed again, and the difference in the two weights gave the amount of water used. The mouth of the wash bottle was kept closed by a cap to prevent evaporation. The wire was then raised until the lower point came in contact with the surface again. The difference in the two readings of the microscope gave the length of the tube filled by a known mass of water. All air bubbles were carefully removed from the walls of the tube, the iron wire and the rubber cork. The temperature of water was noted both at the beginning and the end of an experiment and was found to have kept constant.

If  $L$  cms. is the distance through which the water surface rises in the tube when  $M$  grammes of water are poured into it at temperature  $(t)$ , then the cross-sectional area  $(A) = \frac{M}{L \cdot D}$ , where  $D$  is the density of water at  $t^\circ\text{C}$ . Three such determinations of the cross-sectional area of the tube gave the following results.

(1) 12.75 sq. cm. (2) 12.74 sq. cm. (3) 12.75 sq. cm.  
therefore mean cross-sectional area of the tube = 12.747 sq. cm.

Hence the ratio  $(m)$  between the mean cross-sectional areas of the reservoirs and the U tube is  $\frac{12.747}{8409} = 15.16$

## II. Calibration of the capillary tube.

Considerable time and labour were spent in finding a suitable capillary tube. Several dozens of tubes were examined, and at last one was selected, which for the purpose of this experiment was found sufficiently uniform. Each tube was washed with (1) concentrated sulphuric acid, (2) water, (3) caustic potash solution, (4) distilled water and was then

carefully dried. A short thread of pure mercury was introduced into it, and the length of this thread was measured by means of a travelling microscope provided with a micrometer screw graduated to  $\frac{1}{100}$  mm. In one of these tubes, the extreme values of the length of the thread differed by less than 1 part in 1500 through a range of about 13 cms. The walls of the capillary tube were less than 1 mm. thick. Consequently this portion of the tube was cut off (the ends were carefully cut square) and the portion was carefully washed with strong nitric acid, distilled water, caustic potash solution and finally rinsed with distilled water. It was then dried in a hot oven and allowed to cool in a desiccator over calcium chloride. After weighing the empty tube, it was filled with pure mercury by immersing it in a trough of mercury. When the tube was quite full, the ends were closed with the forefingers of each hand, and, after the small globules adhering to the outer surface of the tube had been brushed off, the tube with its contents was placed in a beaker and weighed, whence the weight of mercury filling the tube at the temperature ( $t$ ) of the experiment was obtained. Let this weight be called ( $w$ ). The length of the tube ( $L$ ) was measured by means of travelling microscope. The temperature of mercury was taken as that of mercury in the trough. The length of the mercury column is not exactly the length of the tube in consequence of the fingers closing the tube pressing slightly into it, but the error due to this cause in a tube of about 1 mm. diameter is negligibly small. The weight of Hg. was also corrected for the buoyancy of air :

$A$  (Mean cross-sectional area) =  $W/LD$  where  $D$  denotes density of mercury at the temperature ( $t$ ) of the experiment.

The mean radius of the capillary tube = .05783 cms.

The capillary tube was then carefully washed as before, dried in an electric oven, and placed in a desiccator over

calcium chloride. When cold, its ends were drawn out and sealed to prevent dust particles getting into it. It was replaced in the desiccator until required for the experiment.

### *III. Preparation and purity of Materials.*

#### *(a) Water.*

Ordinary distilled water was redistilled by adding a little potassium permanganate and acidifying the solution with a little sulphuric acid. The distillate was redistilled after adding a little barium hydrate, and the first and the last portions of the distillate were rejected.

#### *(b) Methyl Alcohols.*

Chemically pure Methyl Alcohol was allowed to stand in a flask for two days with sufficient quantity of quicklime and was then distilled off. The first and the last portions which passed over were rejected. (B. Pt.  $64.6^{\circ}\text{C}$  approx. at 746.8 mm.)

#### *(c) Ethyl Alcohol*

Chemically pure ethyl alcohol was treated after the manner of Methyl Alcohol. (B. Pt.  $78.2$  approx. at 747.7 mm.)

#### *(d) Benzene.*

Chemically pure benzene was allowed to stand in a flask over fused calcium chloride overnight, and distilled twice. The first and the last portions which passed over were rejected. (B. Pt.  $80.1^{\circ}\text{C}$  approx. at 745.0 mm.)

### *IV. Regulation of Temperature.*

The experiment was conducted in an underground chamber the temperature of which was kept constant by means of a thermo-regulator. A diagram of the arrangement for regulating the temperature is given in fig. 3 at the end of the paper.

The thermo-regulator consisted essentially of two strips of metals of different expansibility rivetted together and wound into a spiral as suggested by Ostwald in his "Physico-Chemical measurements." An ordinary Breguet's metallic thermometer was adapted for the purpose. The spiral of the thermometer was composed of three metallic strips of silver, gold and platinum, soldered together so as to form a single ribbon. The silver strip, which is the most expansible was placed inside, the platinum one outside and the gold one between. The spiral had 15 turns with an average diameter of about 0.7 cms. and the length of the pointer was about 6 cms. As the spiral wound or unwound itself with a change of temperature, the tip of the pointer moved through a distance of about 3 mm. for each degree variation of temperature. A brass upright provided with a binding screw was fixed to the base of the instrument near the circumference of the dial. This upright was also provided with another brass screw with flat end, which could be moved backwards and forwards, parallel to the plane of the dial and tangentially to its circumference. By screwing this backward or forward, the distance between the tip of the pointer and the flat end of the brass screw could be finely adjusted. As the temperature rose, the tip of the pointer came in contact with the flat end of the brass screw, and an electric circuit composed of the battery E, the electro-magnet A, and the spiral G, was closed. The electro-magnet A having become excited attracted the iron cross piece B, attached to one end of a wooden rod N hinged at F, and broke the heating circuit consisting of six electric lamps L by pulling out one end C of the thick iron wire M out of a mercury cap. The wire M was bent as shown in the figure, and was carried by the wooden lever E. As the temperature fell, contact between the tip of the pointer and the brass screw was broken, and the electro-magnet A became unexcited. The lever E dropped by its own weight, and again the heating circuit was made. By adjusting the distance between the tip of the pointer and the end of the brass screw the temperature of the underground room could be maintained constant within  $0.03^{\circ}\text{C}$ . This was tested for a period of nearly 3 hours. To diminish sparking between the pointer and the brass screw, a condenser not shown in the diagram was connected in parallel with the spark gap. The air of the room was kept well stirred by means of an electric fan not shown in the diagram. The Breguet's thermometer was covered with a cylindrical wire gauze cage to protect its pointer against disturbances arising out of air currents. This method of screening the instrument proved satisfactory.

*V. Manipulation of the Method.**(a) Arrangement of apparatus.*

The arrangement of apparatus is shown in the diagram (fig. 4, at the end of the paper); XY is a rectangular piece of wood provided with two handles by means of which it can be clamped firmly in position by means of a retort stand supported on an iron tripod provided with levelling screws. M is a glass tube about 0.6 cms. in diameter rigidly fixed to XY and bent at right angles as shown in the diagram. It is closed at its lower end by means of a rubber cork through which passes the capillary tube E. The other end of the glass tube M is connected to a T tube. One limb of this T tube is connected to the pressure regulator BC through a stop-cock G, and the other to one of the reservoirs of the manometer through the stop-cock H. The pressure regulator BC simply consists of two glass tubes of fairly large bore connected together by a thick rubber tube. One of these tubes (C) was kept fixed in position by a retort clamp and the other B was fixed to the carriage of a cathetometer, and could be moved up or down. The micrometer screw of the cathetometer enabled this up and down motion to be made as gradually as required, and hence the final adjustment of the pressure could be made accurately. By opening the stop-cock F, the air above C could be put in communication with the atmosphere. A sharp and distinct mark E was etched on the surface of the capillary tube, the walls of which were less than 1 mm. thick. A is a micrometer screw (a spherometer screw whose pitch was equal to .5 mm. was used; the circumference of its disc was graduated into 100 parts) which when rotated raised or lowered a brass rod R through two well-fitting semi-circular slots rigidly fixed to the plate XY. To the lower end of this brass rod was rigidly fixed a binding screw, which carried an L shaped piece of glass rod. The shorter limb of this glass rod was drawn out into a very fine point V, and its distance from the longer limb was about 5 cms. This

L shaped piece of glass rod served, as will be described presently, to measure the vertical distance of the mark E on the capillary tube below the free surface of the liquid. The liquid under experiment was contained in a carefully cleaned rectangular glass vessel supported on a wooden rising platform Z. The platform could be raised or lowered gently and gradually by means of a nut N, and then clamped securely in position by a screw shown in the diagram. Its base was screwed firmly to the table to prevent its shaking or displacement as the nut N was rotated. The meniscus in the capillary was viewed by means of a microscope D, properly levelled and adjusted so that its optic axis was horizontal. Its focal range was about 4 cms. The readings of the manometer were taken by means of a comparator provided with a micrometer graduated to  $1/200$ th of a millimetre. The comparator was properly levelled and was placed at a distance of over 1.5 meters from the manometer. Three readings were taken for each position of the interfacial meniscus in either limb of the manometer—one reading on the top of the meniscus and the other two on the divisions of the scale between which the meniscus stood, whence the fractions of a mm. were calculated to two decimal places.

*(b) Adjustments.*

The axes of the reservoirs and the limbs of the U tube having been tested for parallelism by a method already described under section I (Manometer), the manometer was set vertical in two mutually perpendicular planes with the help of a plumb-line by adjusting the levelling screws at the base of the instrument. The axis of the brass rod R carrying the L shaped piece of glass rod was also adjusted vertical in two mutually perpendicular planes with the help of a plumb-line by adjusting the levelling screws of the iron tripod which supported the retort stand firmly holding the wooden plate XY. This adjustment was further tested by hanging freely

a small plummet by a fine thread as close to the brass rod R as possible. A Cathetometer telescope placed at a distance of about two metres, and carefully levelled so that its pillar was accurately vertical, and its telescopic axis horizontal, was used to view the rod and the plumb-line thread simultaneously. One of the cross-wires of the instrument was set vertical by making it coincide with the image of the plumb-line thread. The telescope was then slightly rotated so that its vertical cross-wire fell on the axis of the brass rod R. If necessary, the levelling screws of the iron tripod were adjusted until the axis of the rod R and the vertical cross-wire of the telescope were accurately parallel. A similar adjustment was made in another plane perpendicular to the previous one. This latter adjustment slightly affected the previous one, and the two were repeated alternately until the axis of the rod R was vertical in both the planes. (In practice, it was found more convenient and economical as regards time, to use two Cathetometer telescopes and two plumb-lines to make the adjustment described above in two mutually perpendicular planes). After the axis of the rod R had been set vertical, the levelling screws of the supporting iron tripod were not disturbed. The capillary tube (E) which had been carefully cleaned, washed, dried and sealed as described at the end of section II was fixed in position by a rubber cork, so that its upper sealed end rose about half a centimetre above the surface of the cork. This sealed end was broken open before the cork was inserted into the tube M. The Capillary was then adjusted accurately vertical in two mutually perpendicular planes with the help of a plumb-line hung close to it by adjusting the rubber cork only. This adjustment was further tested as in the case of the rod R by means of two Cathetometer telescopes placed in two mutually perpendicular positions. The rubber cork was then made air tight by paraffining it carefully by means of a soft brush near the walls of the capillary and the edges of the tube M. After paraffining, the capillary tube was



tested again for verticality to make sure that it had not been disturbed during the process.

A Microscope capable of swinging about a vertical axis was carefully levelled so that its axis of rotation was accurately vertical and its optic axis horizontal. When so adjusted the microscope remained quite level when swung round in any direction, as was shown by a spirit level fixed to the top of the microscope tube. One of the cross-wires having been adjusted horizontal it was then focused on the mark E on the capillary. It was then swung round so as to view the fine tip (V) of the shorter limb of the L shaped piece of glass rod. The binding screw was loosened a little, and the glass rod was rotated, until the tip (V) was distinctly in focus, and there was no parallax between its image and the horizontal cross-wire. When this was secured, the tip V and the mark E were at the same distance from the vertical axis of the microscope, which could then be focussed on either by simply swinging it round. The glass rod was firmly clamped. The tip V was then raised by rotating the micrometer-screw head (in this case it had to be moved anti-clockwise) until the horizontal cross-wire of the microscope just touched the upper surface of the tip V. The reading of the pointer on the micrometer screw disc was then noted. If by accident the micrometer screw was raised too far up, it was turned down and then raised again to the right position. As the tip (V) had to be raised subsequently through a known distance by turning the screw, this precaution was necessary in order to avoid the error due to its "back lash."

(c) *Making an observation.*

Having noted the zero reading (*i.e.*, the reading when the mark E on the capillary and the top of V were at the same level), the micrometer screw-head was given exactly 20 complete rotations, so that the mark E was vertically lower by one centimetre than the top of V.

A rectangular trough of glass, carefully washed first with strong nitric acid, then with distilled water, then with a solution of caustic potash and finally rinsed with specially distilled water, was placed on the platform Z, and filled with specially distilled water within half a centimetre of the top. The platform was then raised until the lower end of the capillary was well below the surface of water. The lower sealed end of the capillary tube was then broken by means of an iron crucible tongs which had been carefully cleaned with a file and afterwards made red hot in a blowpipe flame. The object in breaking the sealed end of the Capillary under water is to introduce water into it which is free from surface contaminations. The platform was then raised further until the top of V just came in contact with a horizontal portion of the water surface. Contact was secured when the image of V formed by reflection in water coincided with itself. The reflected image was seen with the help of a powerful magnifying glass. Another point to consider was the distance of the point of contact of V with the liquid surface from the walls of the containing vessel, the longer limb of the L-shaped piece of glass rod, and the capillary tube. T. W. Richards (J. A. Chem. Soc., Vol. 37, Part II, 1915) has observed that the bottom of the meniscus in a cylindrical tube about 4 cms. in diameter was horizontal. N. E. Dorsey (Phil. Trans., pp. 369 and 134, 1897) has observed that the effect of the capillary rise against the edges of a plate dipping in water extended to 4 cms. from its edges. Consequently, it was arranged so that the point of contact was in the centre of the trough (12 cm.  $\times$  10 cms.  $\times$  10 cms. approx.) and was not less than 4 cms. away from the capillary or the longer limb of the L-shaped glass rod. The top of the trough was covered with a carefully cleaned iron plate into which slots had been cut to receive the capillary, the glass rod and a thermometer. This reduced the evaporation of the liquid, so that it was quite inappreciable in the course of an

observation and also prevented the contamination of the liquid from atmospheric impurities.

A microscope D, carefully levelled so that its optic axis was horizontal was focussed on the mark E through the walls of the rectangular vessel with plate glass sides through which good definition could be obtained.

A comparator provided with a micrometer screw graduated to  $1/200$ th of a mm. was carefully levelled, so that its pillar was vertical and its telescopic axis remained quite horizontal in all positions, as it was swung round. It was placed at a distance of over a metre from the manometer, and the positions of the interfacial menisci in either limb were read on the respective adjacent scales. Three readings were taken for each position of the meniscus—one on the top of the meniscus and the other two on the divisions of the scale between which the meniscus stood. The stop-cock F was then closed and stop-cocks H, G and I were kept open. The tube B of the pressure regulator was then raised until the bottom of the meniscus coincided with the mark E as seen through the microscope D. Considerable difficulty was experienced at first owing to the interfacial and the capillary menisci adjusting their curvatures to meet a portion of the applied pressure. (Properties of Matter, Poynting and Thomson, p. 142.) The interfacial meniscus J sometimes became concave and occasionally showed a point of inflection. The meniscus K behaved similarly when the stop-cock F was opened and the additional pressure released. Gently tapping the tubes near the menisci had practically no effect. On this account, at first the different values of the manometric readings for the same depression on the capillary meniscus below the free surface did not agree amongst themselves, and differed by 2 or 3 and sometimes as much as 4 units in the first place of decimals. This difficulty was overcome by closing the stop-cock H, and slipping on a rubber tube to the nozzle of the reservoir I. By blowing gentle puffs of air by

the mouth, the interfacial menisci were made to move up and down several times; the amplitude of these movements was adjusted so as to die away gradually; the tubes were also kept tapped gently all the while. After this treatment the interfacial menisci were observed to have recovered their normal shape. The stop-cock H having been opened, the rubber tube P of the pressure regulator BC was pinched several times, which caused the meniscus E to jump up and down. The pinching was adjusted so that the amplitude of these up and down movements died away gradually. Care was taken that the meniscus always came to rest at the end of a downward movement. At the end of this process, it was usually found that the pressure had to be readjusted. The up and down movements of the menisci and the re-adjustment of pressure had to be repeated alternately twice or thrice before the position of the capillary meniscus became constant at E. During the final stage of these adjustments, the pressure was regulated by means of the micrometer screw attached to the carriage of the Cathetometer microscope to which the tube B was firmly fixed. If by accident, the meniscus was lowered below the mark E, it was always raised one or two millimetres above E by lowering the tube B, and was then depressed again so that the mark E was just on the bottom of the meniscus. The procedure already described above was observed to make sure that the menisci did not meet the altered conditions of pressure by changing their curvatures only. The meniscus having been adjusted at E, the tube B was firmly clamped in position. As the distance between the centre of the meniscus and the mark E was less than one and a half millimetre, and the microscope (having a focal range of about 4 cms.) was always levelled horizontal, parallax between the meniscus and the mark E had little effect on the adjustment. The positions of the interfacial menisci on their respective adjacent scales were then read again. From this and the

previous reading of the manometer the excess of pressure applied to the meniscus E was calculated according to equation III, sec. I (manometer).

Before taking the second reading of the manometer, the point of contact of the tip V with the liquid surface was examined to make sure that it had not been affected by the evaporation of the liquid. One observation in general did not take more than 10 minutes, and during this interval it was found that with the proper covering arrangement, the effect of evaporation was quite inappreciable.

The stop-cock F was opened and the platform Z was raised or lowered to throw out the first adjustment. The observation was repeated again as described above. In this way ten independent observations with each of the liquids under experiment were taken for the same depth of the point E below the free surface of the liquid. The manometric readings obtained for any liquid were concordant to 2 decimal places, and showed a variation of a few units in the 3rd place of decimals. Results are given below for water, methyl Alcohol, Ethyl Alcohol and Benzene.

#### *Calculations.*

The formula to be employed is:—

$$T = \frac{1}{2} \text{ gr} [\overline{P - nd} + \frac{1}{2} \text{rd}] \quad \dots \text{ (A)}$$

Substituting the value of P from (iii), p. 3, this becomes:—

$$T = \frac{1}{2} \text{ gr} \left[ Q(S_a - \frac{m-1}{m} S_w) - hd + \frac{1}{2} \text{rd} \right]$$

where:—

Q=change in the difference of level between the meniscuses in the manometer.

$S_a$ =density of aniline saturated with water at the temperature of the experiment.

$S_w$ =density of water at the temperature of the experiment.

$m$ =ratio between the cross-sectional areas of the reservoirs and the U-tube.

$h$ =depression of the liquid meniscus in the capillary below the free surface of the liquid.

$d$ =density of the liquid at the temperature of the experiment.

	Water	Methyl Alcohol.	Ethyl Alcohol.	Benzene
$g$	980.00 cm sec <sup>-2</sup>	980.00 cm sec <sup>-2</sup>	980.00 cm sec <sup>-2</sup>	980.00 cm sec <sup>-2</sup>
$r$	0.5783 cms	0.5783 cms	0.5783 cms	0.5783 cms
$Q$	42.501 "	19.301 "	18.444 "	22.358 "
* $S_w$	1.0127	1.0124	1.0125	1.0126
$S_w$	99586	99573	99581	99581
$m$	15.16	15.16	15.16	15.16
$h$	1.0000 cms	1.0000 cms	1.0000 cms	1.0000 cms
$\dagger''d$	99586	7820	7813	8698
$t$	29.40°C (temperature)	29.79°C	29.58°C	29.54°C
$T$	71.52	23.30	21.32	28.10
(in dynes per cm)				

\*The density of aniline saturated with water was found to be equal to 1.0126 at 29.50°C, (see page 4). From this its value at the actual temperature of experiment for any liquid, (which temperature differed slightly from 29.50°C, the difference not exceeding 3°C in any case) was calculated by applying the formula —

$$\frac{d_t}{d_t'} = \frac{1-at}{1-at'}$$

where  $a$  denotes the coefficient of cubical expansion (0.00850), of pure aniline, it was assumed that for such a small difference of temperature, the coefficient of cubical expansion of aniline saturated with water may be safely taken as equal to that of pure aniline.

$\dagger''$ The densities of Benzene, ethyl and methyl alcohols at their respective temperatures of experiment were calculated from their known values at 20°C, 15°C and 15°C obtained from Kaye and Laby's Tables by applying the formula —

$$\frac{d_t}{d_t'} = \frac{1-at}{1-at'}$$

where  $a$  denotes the co-efficient of cubical expansion of the liquid concerned taken from the same tables

*Results.*

The surface tension of water at 29.40°C as found by this method = 71.52 dynes cm. If the effect of variation of temperature on surface tension be represented by a linear formula of the form  $T = T_0(1 - at)$  and the value of  $a$  taken to be 0.0020 (Dorsey, Phil. Mag., 1897), the surface tension of water at 15°C works out to be 73.79 dynes cm.

The surface Tension of Methyl Alcohol, Ethyl Alcohol and Benzene at 29.8°C, 29.6°C and 29.5°C respectively as found by this method are 23.30 dynes cm. 21.32 dynes cm. and 28.10 dynes cm. respectively.

This method is more sensitive than the ordinary capillary method in which the capillary rise is measured directly. For example with a capillary of .57 mm. radius as used in this experiment, the capillary rise would have been about 2.6 cms. This rise was virtually increased to 3.6 cm. by depressing the meniscus a centimetre below the free surface of the liquid. But the length actually measured on the manometer was about 42.5 cms, nearly 16 times the capillary rise. This length could have been increased still further by increasing  $m$ , the ratio between the cross sectional areas of the reservoir and the U tube. With a value of  $m = 15.16$ , the mean manometric reading for water uncorrected for the calibration error of the U tube is 42.525 cms. approx. The deviations of the individual readings from the mean (neglecting signs) are :—

Approx. .001 .001, .002, .002, .005, .005, .001, .003, .007, .004, cms. respectively.

The average deviation is therefore .003 approx. The error in the determination is therefore 1 part in 14,000 approx., a degree of accuracy which it is doubtful could have been obtained in measuring a rise of about 2.6 cms. by a Cathetometer microscope.

Similarly the average uncorrected manometric readings for Methyl alcohol, Ethyl alcohol and benzene are 19.285 cms.,

18.428 cms. and 22.382 cms. respectively. The average deviation of individual readings from the mean (neglecting signs) are approx. .002 cm. (methyl alcohol), .002 cms. (ethyl alcohol) and .0026 cm. (benzene). The error in determination is therefore less than 1 part in 9000 in the case of the alcohols and a little over 1 part in 9000 in the case of benzene.

*N.B.*—With a more sensitive form of manometer, a higher degree of accuracy is possible. One of these, known as Lord Rayleigh's Micromanometer, is described in 'Nature of Solution,' by O Jones. The Manometer described in this paper was selected on account of its simplicity combined with a fair degree of sensitiveness, as the object of this paper is to describe a modification of the capillary method rather than to execute a determination of capillary constants.

#### SUMMARY OF THE PAPER.

In this paper, a modification of the ordinary method of measuring surface tension by observing the rise of a liquid in a capillary tube is described. The modification consists in measuring, by means of a sensitive manometer, the pressure which must be applied to the surface of the meniscus in order to depress it to the level of the horizontal surface of the liquid outside. In practice it was found more convenient to depress the meniscus to a mark E (Fig. 4) in the capillary, the depth of which below the free surface of the liquid was known accurately. The pressure was measured by means of a sensitive differential manometer.

The values of the surface tension of water, methyl alcohol, ethyl alcohol and benzene as obtained by this method were:—

71.32, 23.30, 21.32 and 28.10 dynes per centimetre respectively at about 29.5°C.

Some advantages of this method of measuring capillary rise are:—

1. The capillary rise can be measured more accurately by this method with the help of a sensitive manometer than by the ordinary direct method.



2. The surface of the meniscus in the capillary is not exposed to atmospheric impurities.

3. As the meniscus is below the surface of the liquid, its temperature is accurately that of the liquid.

4. As compared with the Jaeger's method of measuring surface tension by bubbling air through a liquid, which is essentially dynamical, it has the advantage of being statical; moreover, it is simpler and involves no stiff mathematical problem or uncertain assumption.

5. It is a convenient method for comparing the surface tension of very dilute solutions, and examining the effect of variation of temperature on the surface tension of a liquid. In the first place, as the meniscus is always depressed to a fixed mark on the capillary, the results are independent of variation in the bore of the tube. Secondly, in the formula ( $d$ ), the density of a liquid occurs only in the 2nd and the 3rd terms. As the density of a dilute solution generally does not differ much from that of the solvent, and the effect of the second term can be further decreased by making  $h$  as small as is compatible with a proper observation of the meniscus, changes in the surface tension of dilute solutions will be almost proportional to changes in the value of  $Q$ .

In the end, I wish to thank my friends and professors for the willing help they gave me in carrying out this experiment.

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BARKAT ALI



FIG. .

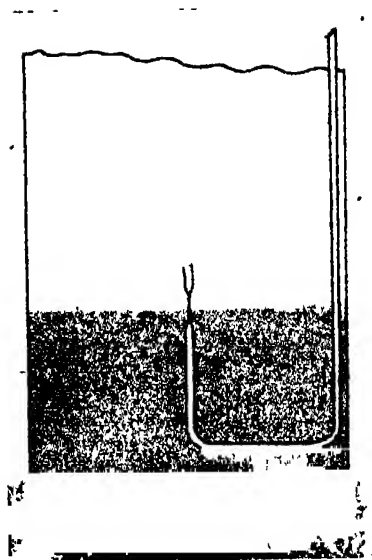


FIG. 11

BARKAT ALI

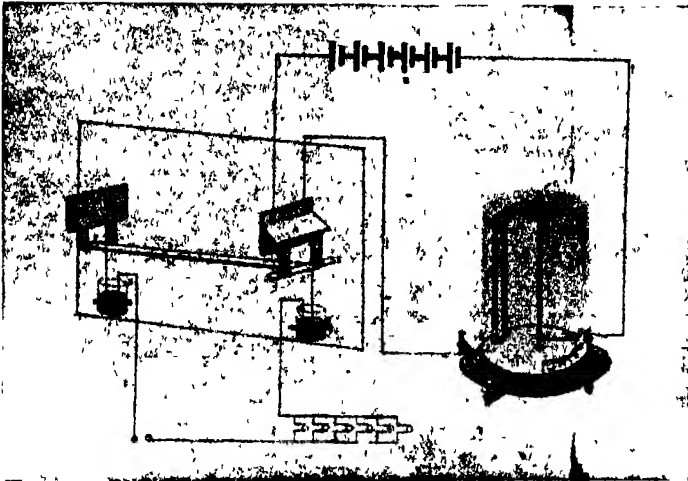


FIG. III.



MARKAL S.L.

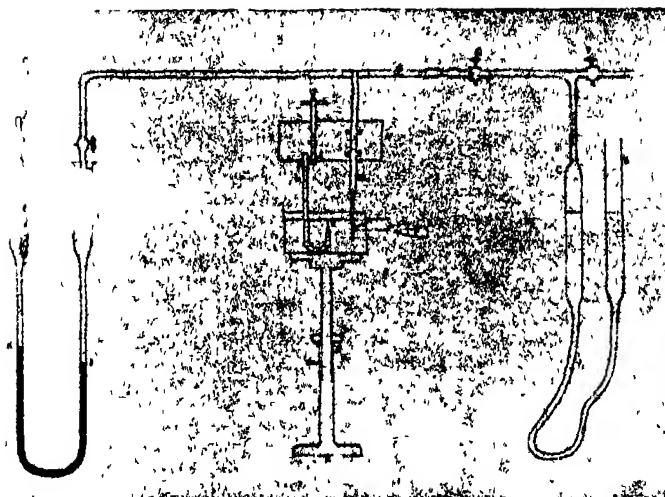


FIG. IV.



## On the Fusion of Crystalline Solids.

BY

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1. The atoms composing a crystal have a definite spatial arrangement and the phenomenon of melting consists in the breakdown of this arrangement accompanied by the mobility of the loosened constituents. The mobile units may be similar atoms as in the case of the majority of metals, "ions" as in the case of fused inorganic salts, single molecules as in "unassociated" organic liquids, or groups of molecules as in water, ethyl alcohol and formic acid.

As distinguished from the phenomenon of vaporization, fusion has one remarkable feature; while the former from either the liquid or the solid state takes place over a whole range of temperature, the latter takes place quite sharply at a definite temperature. We can see in a general way why this should be so. Let us consider a crystal at a temperature a few degrees below the melting point. An atom or group of atoms in the middle of the crystal is surrounded on all sides by other atoms by bonds of varying strength, while a similar atom or atomic group at the surface of the crystal is free on the outside, so that it will be easier to pull out one of those on the surface than one inside. When liquefaction takes place, it always starts at the surface and progresses inwards. When a beam of sunlight is concentrated by means of a lens inside a block of ice, the liquefaction



does not take place in the whole region of the track all at once, but starts at a few slip-planes which are invariably present and progresses from them. When the surface atoms or atomic groups get sufficient energy of vibration, they get loosened. The phenomenon may be compared to the wrenching out of pegs driven on the ground, the vigour of the thermal movement being responsible for the wrenching. When the temperature is such that only a few molecules here and there have sufficient energy of movement to escape, we have only volatalization, and it is only when the temperature gets so high as to cause simultaneous release of a number of molecules at the surface so close to each other that the Van der Waals' attractive force between them is large enough to keep them together, we have fusion to the liquid state. The reason why the melting point is so definite and there is no known case of superheating is to be found in the fact that the melting point is not the temperature at which the structure inside the crystal breaks down all at once, but it is the temperature at which atoms or atomic groups at the *surface* of the crystal become loose.

2. We can divide the attractive forces between molecules into two different kinds, one mainly confined to certain specific directions and the other a general all-round attraction such as is contemplated in Van der Waals' theory. In isotropic liquids, it is the latter that is mainly in operation; in crystals, both play a part, but it is the presence of the former that gives rise to the spatial arrangement of atoms. When the attractive forces are concentrated in certain directions and the forces in other directions are comparatively weak, the crystal will have an open character and on rise of temperature, it will tend to pass directly from the solid to the vapour state as for example carbon and many organic crystals like naphthalene; on the other hand, when the attractive forces are practically uniform on all sides, the crystal will have a close-packed structure, the substance will

remain liquid over a large range of temperature and the vapour-pressure at the melting point of the substance will be quite low. We may also expect such substances to be soft. Many metals fall into this class.

3. It is clear that in general, it is the loosening of the directional bonds that causes the melting of the crystal. In crystals of many compound substances and of some elements like bismuth, sulphur and carbon in the form of graphite, the bonds which lock an atom or molecule in different directions are not of equal strength. In these cases, it is the strength and number of the *strong* bonds that will determine the melting point. Some bonds may be loosened at temperatures far below the melting-point. The transformations from one crystal form to another exhibited by many crystals afford definite evidence of this. Melting does not take place until the strongest bonds are broken. In the homologous series of paraffins, the melting point rises regularly as we go up the series. *A priori* we have no reason to expect an increase of binding strength in the higher members of the series, but in order to free a molecule containing a larger number of atoms, it requires the simultaneous release of a larger number of bonds and hence the kinetic energy required for the release should be higher. Again Sir W. H. Bragg has shown that the structures and the nature of the bonds in both naphthalene and anthracene are the same; yet the melting point of naphthalene is  $80^{\circ}\text{C}$ , while that of anthracene is  $216.5^{\circ}\text{C}$ .

The case of liquid crystals is of interest in this connection. When a long molecule has one or two comparatively strong bonds localised at its ends, the weaker bonds may all be destroyed before the end-bonds give way and the molecule may acquire considerable sideways freedom of movement leading to a breakdown of the space-lattice. The clearing point of the liquid crystal would correspond to the final breaking-up of these stronger end-bonds.

#### 4. *Latent Heat of Fusion.*

We do not possess a satisfactory theory of the latent heat of fusion even of the monatomic metals crystallizing in the cubic system. Many attempts have been made notably by Ratnowsky,<sup>1</sup> Allen,<sup>2</sup> Honda,<sup>3</sup> and Lindemann<sup>4</sup> to formulate a suitable theory. The present position of the question has been clearly and succinctly stated by Lindemann. He points out that in the case of the monatomic solids which expand on fusion, nearly half the latent heat is work done against the cohesive forces. He considers the energy content of a liquid at the melting point  $T_m$  to be given by an expression of the form

$$3R \int_0^{T_m} f(\theta_2/T) dT$$

similar to Debye's expression for the heat content of a solid. Here  $\theta_2$  denotes the "characteristic" temperature of the liquid and Lindemann argues that owing to the greater distance between the atoms in the liquid, the restoring force on an atom would be smaller than in the solid and hence the atomic frequency  $\nu$  and the characteristic temperature  $h\nu/R$  would be lower. The excess of the latent heat over the work done against the cohesive forces is taken to be given by

$$3R \int_0^{T_m} [f(\theta_1/T) - f(\theta_2/T)] dT$$

where  $\theta_1$  is the characteristic temperature of the solid. One considerable difficulty in applying Debye's theory<sup>5</sup> to the heat content of a liquid is that unlike as in a solid where the

<sup>1</sup> Ratnowsky, *Deutsch. Phys. Gesell. Verh.* Vol. XVI, p. 1033, 1914, quoted by Allen

<sup>2</sup> H. S. Allen; *Proc. Phys. Soc.*, Vol. 28, pp. 204 and 302, 1916.

<sup>3</sup> Honda; *Phil. Mag.*, Vol. 45, 1923.

<sup>4</sup> Lindemann; *Phil. Mag.*, Vol. 45, 1923.

<sup>5</sup> Jeans; *Report on Radiation and Quantum Theory.*

number of possible independent vibrations between wavelengths  $\lambda$  and  $\lambda + d\lambda$  is  $12\pi\lambda d\lambda^{-1}$ , of which two-thirds are waves of distorsion and one-third waves of compression, the number of possible independent vibrations in a liquid can only be  $4\pi\lambda^{-1} d\lambda$  since distorsional waves are ruled out, and hence in order to get  $3N$  degrees of freedom for  $N$  atoms, the upper limit of frequency and the characteristic temperature have to be higher in the liquid than in the solid (in spite of the greater compressibility of the liquid). Indeed, Allen has shown that in the case of liquid mercury, the characteristic temperature as calculated from its compressibility is  $205^\circ$  K while that of the solid calculated by Lindemann's formula is  $96^\circ$  K. In view of this discrepancy, the application of Debye's theory to liquids is of doubtful validity. Moreover, Lindemann's theory contemplates only isotropic binding.

5. Approaching the question from a different standpoint, it is of interest to enquire whether definite quantities of heat are associated with the breaking up of definite types of bonds. In the case of many organic substances, the mobile units in the liquid state are single molecules and the same bond is often repeated in other crystals. For example, the molecular heats of fusion of naphthalene and anthracene are  $4.5 \times 10^3$  calories and  $6.9 \times 10^3$  calories respectively. It is known from Bragg's X ray analysis of these two crystals that the structures of the two compounds are similar, and that the  $\alpha$ -hydrogens lie up against the Carbon-atoms of the next molecule while the  $\beta$ -hydrogens are in juxtaposition with similar atoms of neighbouring molecules. The force between molecule and molecule is mainly across the  $\alpha$ -hydrogens as is shown by the fact that the cleavage-planes of the crystals lie across the junctions of the  $\beta$ -hydrogens. The number of  $\alpha$ -hydrogens in naphthalene and anthracene are in the ratio of 2:3 and since the latent heats of fusion are also in the same ratio, the main part of the work of fusion has to be done in breaking

the  $\alpha$ -hydrogen bonds. The bond between hydrogen and hydrogen is much weaker. The molecular heat of fusion of benzene is  $2.37 \times 10^3$  calories which is nearly half that of naphthalene, while that of cyclohexane, a molecule of similar constitution to benzene, but whose crystal can have only hydrogen to hydrogen bonds, is  $0.49 \times 10^3$  calories. The crystalline form of benzene is different from that of naphthalene, but as its structure has not been completely analysed, we do not know the nature of the bonds in the crystal. From analogy to naphthalene and anthracene and from the fact that its heat of fusion is nearly one-half that of naphthalene, it is likely that, as bound up in a crystal, two of its six hydrogen atoms are held more strongly than the other four.

In the following table are given the melting points and the molecular heats of fusion of a number of aromatic compounds.<sup>1</sup>

TABLE I

Substance	Melting point	Molecular latent Heat of Fusion
Benzene	5.4°C	$2.37 \times 10^3$ cal
Phenol	41 °C	2.77 „
Nitrobenzene	5.8	2.76 „
Resorcine	110	2.80 „
Aniline	-7.0	1.95 „
Naphthalene	80	4.5 „ = $2 \times 2.25$

<sup>1</sup> The data are taken from Landolt—Börnstein Tabellen

TABLE I—*contd.*

Substance.	Melting point	Molecular latent Heat of Fusion.
Hydrazobenzol ( $C_6H_5 \cdot NH$ ) <sub>2</sub>	13·4	4·21 „ = $2 \times 2·10$
Azobenzol ( $C_6H_5$ ) <sub>2</sub> N <sub>2</sub>	68	4·83 „ = $2 \times 2·42$
Benzil ( $C_6H_5 \cdot Co$ ) <sub>2</sub>	94·9	4·65 „ = $2 \times 2·32$
Benzo-phenone ( $C_6H_5$ ) <sub>2</sub> -Co	48·0	4·31 } „ = $2 \times 2·07$ 3·95 }
Diphenyl ( $C_6H_5$ ) <sub>2</sub>	70·2	4·39 „ = $2 \times 2·20$
$\alpha$ -Nitro-naphthalene	56	4·38 „ = $2 \times 2·19$
$\alpha$ -Naphthylamine	50	3·66 „ = $2 \times 1·83$
Anthracene	217	6·89 „ = $3 \times 2·30$
Anthroquinone	282	7·78 „ = $3 \times 2·59$

It will be noticed that in a large number of aromatic compounds, corresponding to each benzene ring, there is approximately a definite molecular heat of fusion. This can be interpreted as meaning that the strongest bonds which unite molecule to molecule in crystals of the above compounds are of the same kind and are those characteristic of the benzene ring. As is only to be expected, the heat of fusion depends to some extent on the added radical.

When one of the hydrogens in benzene is replaced by a halogen atom, it causes an increase in the strength of binding. When two halogens are introduced, the strength of binding depends on the relative positions of the halogens, being greatest when the two halogens are in para-positions and nearly the same when in the ortho or meta positions.

TABLE II.

Substance	Melting point	Molecular Heat of Fusion.
<i>o</i> -Dichlorobenzene	... —17° 5C	$3.09 \times 10^3$ Cal.
<i>m</i> -Dichlorobenzene	—24° 4C	3.02 „
<i>p</i> -Dichlorobenzene	52° 9C	4.34
<i>o</i> -Dibromobenzene	1° 8	3.02
<i>m</i> -Dibromobenzene	—6° 9	3.16
<i>p</i> -Dibromobenzene	86° 9	4.90
<i>o</i> -Di-iodo benzene	21° 4	3.36
<i>m</i> -Di-iodo benzene	34° 2	3.80
<i>p</i> -Di-iodo benzene	129° 0	5.34

*Summary.*

1. It is pointed out that the definiteness of melting point and the absence of superheating of a crystal are due to the diminished strength of binding of a molecule at the surface of the crystal as compared with that of one inside, and that the crystal begins to disintegrate when the temperature becomes high enough to dislodge the *surface* molecules.

2. The forces between atoms and molecules can be analysed into two, one uniform all round and another specially concentrated in definite directions.

3. A crystal melts when its directional bonds get loosened. The melting point depends both on the number of bonds and the strength of the bonds which attach one molecule to another.

4. An analysis of the heats of fusion of a number of aromatic compounds shows that there is approximately a definite molecular heat of fusion corresponding to each benzene ring. This is presumably connected with the similarity of binding between molecule and molecule. This conclusion is supported by X-ray evidence regarding the structures of naphthalene and anthracene.

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## 2

# The water-spark absorption spectrum of Copper

BY

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The spectrum of copper has been studied by various methods from  $1.84\mu$  down to the extreme X-ray region. Some of the lines have been classified in a series of doublets by Kayser and Runge,<sup>1</sup> by Rydberg and by Dunz. An extensive discussion of the spectrum of copper has been made by Hicks in relation to the "oun." It appears that some of the chief lines can be arranged in groups of doublets, similar to those of alkali metals, but many important lines remain to be classified. The number of lines in the spectrum of copper is so large that it is not probable that even excluding the case of enhanced lines, the lines due to a neutral atom can all be included in a series of doublets.

The writer has studied the spectrum of Cu. in a water-spark. The spectrum of high-frequency spark between metallic electrodes under water has been previously studied by Konen<sup>2</sup> and Hale<sup>3</sup> and more recently by Victor Henri,<sup>4</sup> Hulbert<sup>5</sup> and Stücklen,<sup>6</sup> and by Sur and Majumdar in this laboratory.

The sparking cell, shown in fig. 1 and employed in these experiments, is in certain respects different from those used

<sup>1</sup> For references to the Literature of Spectrum of Copper, vide Fowler, Report on Series in Line Spectra, p. 109.

<sup>2</sup> Konen *Aun der Phys.*, 9, 779, 1902

<sup>3</sup> Hale, Publication of the Yerkes Observatory, 3rd part, 2 (1907)

<sup>4</sup> Victor Henri, *Proc Roy Soc A* 105, pp. 668-69, 1924.

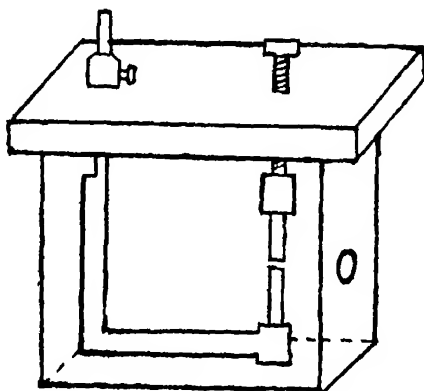
<sup>5</sup> Hulbert, *Phys Rev.* 24, 129-33, 1924

<sup>6</sup> Stucklen, *Zeits f Phys* 30, 24-39, 1924



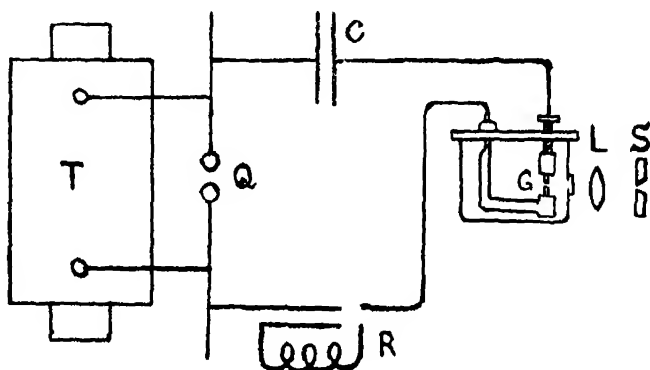
by previous experimenters, and has been designed by Messrs. Sur and Majumdar in this laboratory.

*Fig. 1.*



A hole, 1 cm. in diameter, is bored in a rectangular glass cell, somewhere in the middle of one of its faces, and is closed with a quartz plate cemented with de Khotinsky cement. The top of the vessel is covered by an ebonite plate, 1 cm. in thickness. It carries two supports for the electrodes; which are fixed in sockets and tightly held in position by means of screws. The upper support is movable, and can be fixed in any desired position. A suitable distance between the electrodes is 1 mm. or so. The vessel is filled with distilled water and the connections are made as shown in fig. 2.

*Fig. 2.*



T is an induction coil of capacity  $\frac{1}{4}$  k.w. It is worked by a mercury interrupter. The secondary terminals are connected

to an air spark gap Q. The spark gap Q, the condenser C, the water-spark gap G, and the self-inductance R are connected so as to form a high-frequency circuit. By properly adjusting the air gap discharge passes between the electrodes immersed in water. The condenser needs some special mention. It was prepared from glass plates 5 mm. thick, and cut into rectangular pieces  $20'' \times 10''$ . Each glass plate was coated with shellac on both the faces, on a margin of two inches in width on all sides. Any required capacity could then be formed by putting a suitable number of thin zinc sheets of dimensions  $16'' \times 6''$ , separated by the glass plates. Alternate zinc sheets connected together formed the two terminals of the condenser. Such a condenser can be easily set up; its capacity can be varied within wide limits and any glass plate ruptured during the experiment can also be easily replaced. The capacity of the condenser used was about  $.001 \mu F$ . This capacity was found to be very suitable for producing the discharge; any higher capacity demands a higher rate of supply of power as has been noted by Anderson.<sup>1</sup>

The spark was focussed on the slit of a small quartz spectrograph by a quartz lens L. For photographing the spectrum Kodak Seed 40—plates and Wellington Anti-screen plates sensitized according to the method described by Lyman<sup>2</sup> were used. As the spark takes place with explosive violence, the distance between the spark-gap and the quartz-window could not be made less than a centimeter and a half. Any attempt to bring the spark-gap nearer resulted in the cracking of the window.

The core of the electrodes is evidently a region of high temperature and pressure, as indicated by the rapid disintegration and deformation of the electrodes, and also by the fact that the thin quartz-window cracked due to the pressure developed in the discharge. This region consequently emits

<sup>1</sup> Anderson, *Astrophys. J.* 59, 76-96, 1923.

<sup>2</sup> Lyman, *Nature*, 1923.

a continuous spectrum. But surrounding the central one is also an outer region, which contains the vapour of the metal forming the electrodes. Under ordinary conditions, a continuous spectrum interspersed with absorption lines is obtained. Sometimes emission lines also appear. The character of the lines however changes enormously with the conditions of the experiment and depends upon several factors.

(1) *Self-inductance*—The effect of including self-inductance is to obliterate the reversals and to give rise to emission lines in their places. In the oscillatory circuit with the given capacity and transformer, if a self-inductance of magnitude  $2 \times 3.7 \times 10^4$  cms. were included, the reversed lines became indistinct; nearly all the lines of Cu. appeared in emission on a continuous background when the self-inductance was increased to  $3 \times 3.7 \times 10^4$  cms. (Fig. 3*b*). An examination of the plates indicated that the most important pair of lines  $\lambda\lambda 3273.97$  and  $3247.55$ , which are the first to appear as absorption lines, are also the first to be influenced by the self-inductance. This points to the conclusion that the outer envelope of the vapour of metal is entirely removed when sufficient self-induction is put in the circuit.

The self-inductances used were prepared by winding bare copper wire 2.5 mm. in diameter on wooden bobbins dipped in molten paraffin oil. The bobbins were 30 cms. long and 5.5 cms. in diameter. Each spule contained 60 turns of wire and produced a self-induction of  $3.7 \times 10^4$  cms. for steady currents.

(2) The form of the electrodes employed has also a marked influence upon the character of the spectrum. The

discharge becomes more powerful and abrupt with pointed electrodes, and in the spectrum, emission lines appear in place of absorption lines. Flat electrodes seem to be very favourable for the production of absorption spectra. Fig. 3 (c) and (a) show the spectra produced with pointed and flat electrodes respectively. The difference is probably due to the fact that in the case of the pointed electrodes, the discharge passes between a very small area, and very little of the metal is chipped off from the electrodes, and consequently the outer envelope is not formed.

(3) The nature of the discharge depends on the transformer, *i.e.*, on the rate of power supply. A transformer of large capacity tended to make the spectrum more continuous specially below 2200 Å°U. To obtain the absorption lines in that region it was found best to use an ordinary induction coil worked at about 14 volts. This point requires further detailed study before any definite conclusion can be derived about it.

The conditions for securing a good absorption spectrum being thus known, the spectrograms that were taken extended down to 1950 Å°U. The wave lengths of the absorption lines obtained were determined by comparison with a copper arc-spectrum. The pair of lines 3273·97 and 3247·55, constituting the first member of the principal series of Cu. was obtained as very sharp reversal lines. The second member of this series did not appear as a doublet, but as a single diffuse absorption line, distinct though weak. The lines, that were obtained in absorption, are listed below :—

λ. (I. A.)
(Hasbach)
3273·97
3247·55
2246 98
2242·60
2230·07
2227·74

2215·65 }  
 2214·56 } Not resolved in the spectroscope.  
 2199·65

2192·24

2179·37

2165·06

2135·92

2130·70

2025·1 Wave-length measurement uncertain.

In this group occur some pairs with constant frequency difference as noted below :—

$\lambda$ (I.A.)	$\nu$	$\Delta\nu$
2227·74	44888·54	
2199·65	45461·77	573·23
2192·24	45615·45	
2165·06	46188·10	572·65
2227·74	44888·54	
2192·24	45615·45	726·91
2199·65	45461·77	
2165·06	46188·10	726·33

Recently the constitution of copper arc-spectrum has been studied by Shenstone<sup>1</sup> in low-voltage arc and in absorption. His results of the absorption-experiment do not quite agree with that of the author. Though he has calculated several combinations, using a term  $md. = 51105\cdot5$ , the nature of many terms remain yet unexplained. The large number of arc lines, still awaiting classification into series, makes it clear that the spectrum is very complex. It seems to involve combinations of the nature of  $pp'$  and  $dd'$ , and probably quartet terms are also involved in the constitution of the spectrum.

The writer takes this opportunity of offering his best thanks to Prof. M. N. Saha for his interest in the work.

ALLAHABAD, }  
*June, 1925.* }

<sup>1</sup> Shenstone, Phil. Mag., 49, 051-062, 1925.

# Experimental Study of the Elastic Impact of Pianoforte Hammer

BY

R. N. GHOSH, M.Sc., and J. N. DEY, M.Sc.

§1. It has now been definitely settled<sup>1</sup> that the duration of contact of a pianoforte hammer when it impinges upon a steel string under tension is finite in comparison to the period of vibration of the string. The time of contact depends upon the tension, length of the string, the striking distance, the mass of the hammer, and the elasticity of the hammer felt. To some the influence of elasticity upon the duration of contact is negligible, while it must be admitted that the piano-builders take the fact into consideration since the different hammers of different octaves, have not only different masses, but differ in respect of elasticity in as much as they possess thicker or thinner layer of felt.<sup>2</sup> The present paper contains an account of the experimental determination of the duration of contact with different hammers and steel wires, and a comparison has also been made of the results with the theoretical formula.<sup>3</sup>

## § 2. *Experimental arrangement.*

In order to determine the time of contact, a sonometer is fixed vertically quite rigidly, a horizontal slit S is placed quite near the point of the wire at which the duration of

<sup>1</sup> A complete bibliography on the subject will be found in Mr. W. H. George's papers, *Phil. Mag.*, Vol. 47, p. 591 (1924), Vol. 48, p. 48 (1924), etc.

<sup>2</sup> The elastic bending of the hammer rod may also affect the duration of contact.

<sup>3</sup> *Phil. Mag.*, Vol. 49, p. 124 (1925)

contact is to be measured. Powerful light is obtained from arc lamp placed on an adjustable table. The arrangement is shown in Fig. 1.

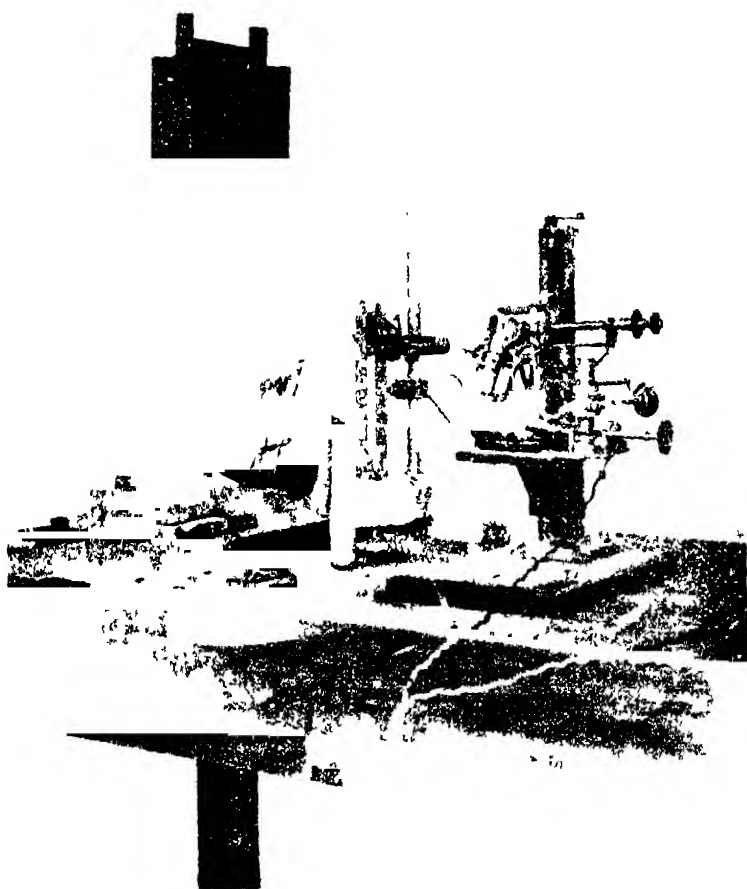


Fig. 1

A particular point is struck by the hammer and the shadows of the point of the string, and the hammer, are

photographed by a vertically falling plate which records the approach, the contact, and the separation of the hammer from the string. The trace of a vibrating tuning fork simultaneously enables us to measure time. The hammer system was separate from the sonometer; it consisted of a hammer head attached to a rod hinged to a piece H, and the blow was given by pressing a lever system which imparted a momentum to the hammer. The whole system is shown in the figure Plate I, H, and is almost the same as the pianoforte key. The hammer head is shown near the slit S.

*Dimensions of the apparatus.*

The length of the string was about a metre, it was kept under tension over two wooden bridges tipped with ivory. The string was a steel wire, and in different experiments different diameters were used. The shape of the hammer head is clearly shown in the photograph (Fig. 1); it is about 6 cm. long and 4 cm. broad, the length of the wooden rod (pine) to which the hammer head is fixed, is about 7 cm. and the diameter is about 6 mm. All the materials were borrowed from a local piano-tuner, and the wires, hammers, rods, etc., were those actually used in different octaves of the piano. The hammer head was made to strike perpendicularly different points of the string, keeping the total length and tension of the string the same. Since the horizontal slit was adjustable the shadowgraph was easily obtained. Care was taken to keep the parts of the apparatus rigid.

§ 3. *Experiments.*

$m$  = mass of the string per cm.

$M$  = mass of hammer head +  $\frac{1}{3}$  mass of rod.

$T$  = tension,  $l$  = length,  $F$  = frequency.

$\mu$  = elastic strength.

$a$  = striking distance from nearer end.



In order to compare the experimental values with those calculated from formula (6), p. 124, Phil. Mag., Vol. 49 (1925), and Kaufmann's formula, tables have been drawn up showing the different values. Formula (6) in the case of elastic hammer runs as follows:—

$$\phi = \frac{\pi X^{\frac{1}{2}}}{\left(\frac{T}{M}\right)^{\frac{1}{2}} \left(1 - \frac{m}{M} \frac{1}{X}\right)^{\frac{1}{2}}} \text{ app}$$

where  $\phi$  = duration of contact, and

$$X = \left(1 + \frac{T}{\mu a}\right)^{-1}$$

In the case of hard hammer  $X=1$  since  $\mu$  is infinite, and the above formula reduces to Kaufmann's.

TABLE 1.

$T=2.47$  dynes;  $m=0.795$  gm. per cm.;

$l=95.8$  cm.;  $T/\mu=0.56$ ;  $M=19$  gm.

$a$	$\phi$ obs.	$\phi$ cal.	$\phi$ kauf
7.	7.3	7.5	$7.28 \times 10^{-3}$ sec
8.	8.06	8.03	7.78
9	8.56	8.45	8.39
9.5	8.90	8.89	8.66
10.0	9.54	9.33	9.12
10.5	9.64	9.56	9.30

TABLE 2.

$$T = 8.45 \times 10^8 \text{ dynes.}$$

$$F = 100, m = .0211.$$

$$l = 100, M = 7.1.$$

$$T/\mu = .41.$$

$\alpha$	$\phi$ obs	$\phi$ cal	$\phi$ kauf
8	$8.37 \times 10^{-1}$	8.4	8.3
9	9.0 „	8.95	8.7
10	9.3 „	9.4	9.2
11	$1.06 \times 10^{-2}$	9.84	9.66
12	1.16 „	1.04	1.03
13	1.17 „	1.09	1.05
14	1.27 „	1.13	1.11
16	1.4 „	1.24	1.21

} Double  
contact

TABLE 3.

$$M = 8.0, l = 100.$$

$$T/\mu = .376, m = .0211, F = 100.$$

$\alpha$	$\phi$ obs.	$\phi$ cal	$\phi$ kauf
8	$0.91 \times 10^{-1}$	0.92	0.88
9	0.98	0.97	0.93
10	1.02	0.995	0.97
11	1.06	1.05	1.02
12	1.11	1.10	1.08
13	1.20	1.13	1.11

TABLE 4.

$$T = 2.50 \times 10^7, l = 96, F = 94.$$

$$M = 10.2, T/\mu = 1.68, m = .0795.$$

$\alpha$	$\phi$ obs	$\phi$ cal	$\phi$ kauf
6.15	5.45	5.40	$4.94 \times 10^{-3}$
7.0	5.95	5.96	5.4
8.6	6.3	6.5	6.0
9.2	6.6	6.73	6.2
9.85	6.8	6.76	6.25
10.3	7.1	7.12	6.6
10.95	7.5	7.4	6.83
12.2	7.6	7.5	7.10
13.6	7.9	8.1	7.7

TABLE 5.

$$l = 96, T = 2.59 \times 10^7.$$

$$m = .0795, F = 94.$$

$$T/\mu = 0, M = 2.6 \text{ gm.}$$

$\alpha$	$\phi$ obs.	$\phi$ cal	$\phi$ kauf.
10	$2.8 \times 10^{-3} \text{ sec.}$	3.1	3.1
12	3.5	3.6	3.6
16	3.9	4.1	4.1

TABLE 6.

$$T/\mu=0, T=1.35 \times 10^7, l=92.4.$$

$$F=137, M=2.6, m=.0211.$$

$\alpha$	$\phi$ obs	$\phi$ kanf
8.6	$4.3 \times 10^{-3}$	4.1
10	4.6	4.5
13	5.2	5.0

The velocity of impact of the hammer can be determined from the photographs by measuring the tangent of the angle made by the tangent at the point of contact and the linear velocity of fall of the plate from the trace of tuning fork. From the calculated values of the duration of contact and the velocity of impact, the maximum displacement after a time  $\phi/\alpha$  has been calculated from the formula

$$\beta = \frac{v_1 \phi}{\pi} e^{-\frac{K}{4} \phi} (\text{loc cit})$$

this quantity has also been measured from the photographs, and comparison tables have been drawn.

TABLE 7.

$$M=19, l=96, m=.0795.$$

$\alpha$	$\nu_1$	$\nu_1/\nu_2$	$\beta$ cal.	$\beta$ obs
7.5	$3.85 \times 10^{-3}$	1.8	48	44
8.5	2.25	1.35	40	44
9.0	2.05	1.90	47	45
9.5	1.85	1.57	43	43
10.0	1.97	1.30	42	44
10.5	3.47	2.10	47	45
11.0	2.20	1.05	50	51
12.0	1.2	1.58	57	58

TABLE 8.

$$M = 10.2, l = 96, m = .0795.$$

$\alpha$	$\nu_1$	$\nu_1/\nu_2$	$\beta$ cal	$\beta$ obs
6.15	$2.1 \times 10^7$	1.23	36	38
7.0	1.95 „	1.34	37	37
8.6	1.97 „	1.6	40	40
9.85	2.3 „	1.38	50	56
10.3	2.88 „	1.6	56	60
10.95	1.67 „	1.38	39	41
12.2	2.5 „	1.93	49	45
13.6	2.2	1.82	46	46

A few photographs have been reproduced in this paper. Table 9 explains the different figures.

TABLE 9

No	$m$	M	$\alpha/l$	REMARKS
1	0.211	2.6 gm.	10/92	Hard hammer
2	„	7.1	10/100	Elastic
3	„	8.0	13/100	„
4	„	7.1	14/100	„
5	0.795	10.2	7/96	„
6	„	19.0	10.5/96	„
7	„	10.2	12.2/96	„

With hard hammer fig. 2(a) the vibration curve has sharp points, showing the presence of high partials, and the duration of contact is short. While in the case of elastic hammers, the curves are smooth, and the duration of contact is greater than hard hammers. A fuller investigation on the

effect on partials by different types of hammers is in progress and will be communicated in due course.

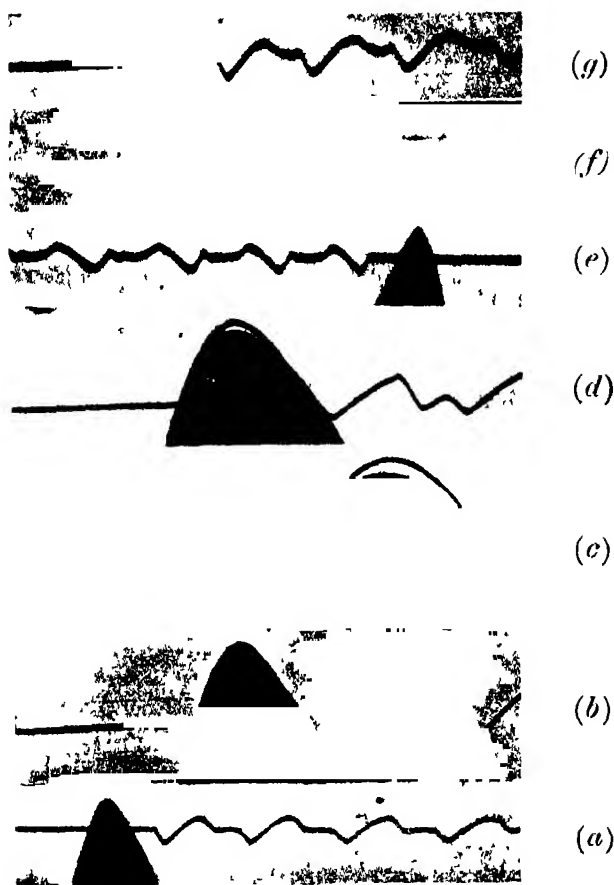


Fig 2

Figs 2(b), 2(c) and 2(d) show the impact on the same string  $m = .0211$  per cm. at increasing distances by two different hammers. When the striking distance is small, *viz.*,  $\frac{1}{10}l$  Fig. 2(b) it will be observed that the string does not leave the hammer before the final separation, while Figs. 2(c) and 2(d) show that the string once leaves the hammer, again comes in contact, and then finally leaves the hammer when the striking distances are  $\frac{1.3}{100}$ ,  $\frac{1.4}{100}$  respectively. With greater distances, photographs show (not reproduced) that the

interval of separation increases. With thicker string, however, the hammer does not make double contact even when the distances are increased to  $\frac{1}{2}l$  shown by figs. 2(e), 2(f) and 2(g). As long as the transverse wave generated by impact does not return after reflection from the longer end, the tension is the same as the pressure between the hammer and the string; when the striking distance is increased, the transverse wave after reflection reaches the hammer before the impact is over, and then the pressure is not the same as the tension. The variation of pressure when the striking distances are large has been calculated by Raman\* and Banerji, and Das,† their curves show the phenomena in details. Fuller discussion will soon follow.

PHYSICS DEPT.,

ALLAHABAD UNIVERSITY.

*16th May, 1925.*

\* Proc. Roy Soc A, Vol 97, p 99 (1920).

† Proc. Ind Assn., Vol. VII, Parts I and II, p 13 (1920).

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## The Polarisation of the Light scattered by some Organic Vapours.

BY

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### *Introduction.*

In two recent papers,<sup>1</sup> one of the authors has developed an approximate theory of the optical anisotropy of molecules which has been found helpful in explaining the broader features of its dependence on molecular structure. For further progress, it was felt desirable to secure more data regarding the polarisation of light scattered by vapours of substances whose molecular structures are known from other considerations and the experiments described in this paper were undertaken with that view. An extensive series of measurements on the polarisation of the light scattered by organic vapours has been recently published by A. S. Ganesan,<sup>2</sup> and another series both as regards intensity and polarisation on methane and some of its homologues by Cabannes and Gauzit.<sup>3</sup> Most of the substances studied by us differ, however, from those of the above two investigations and the apparatus employed also possesses some features of interest, having been designed for work with vapours which require heating for their production. In this paper, we have given a brief account of our experiments followed by a discussion of the results

<sup>1</sup> 'The Structure of Molecules in relation to their Optical Anisotropy.' Part I, Proc. Roy. Soc. A, Vol. 107, p 684, Part II in course of publication.

<sup>2</sup> Phil. Mag Vol. XLIX, June 1925, p 1216.

<sup>3</sup> Journ de Physique, Ser. VI, Tome VI, pp. 182-198 (June 1925).



obtained and of some points connected with the measurement of depolarisation in gases and vapours; the optical anisotropy of the carbon atom and its significance are also considered.

### *Apparatus.*

The main part of the apparatus consisted of a double-bulbed (diameter of bulbs 5 to 6 cms.) glass tube of the form shown in the figure (Fig. 1).<sup>1</sup> Particular care was taken to see that the smaller bulb was blown clear and uniform with no blob or streak at its bottom. After cleaning and drying, a small quantity of the pure substance was introduced into the tube and, after pumping out the air inside, the horn end of the tube was sealed off. The bulbs and tube were painted black leaving only three small windows, two at the sides of the larger bulb for the entrance and exit of the incident light and the third at the bottom of the smaller one for the observation of the scattered track, the stem of the tube serving as a background. Experiments with a glass cross-tube of the kind used by Cabannes and his co-workers showed that it was difficult to secure anything like the satisfactory background obtained with metal tubes fitted with diaphragms. Since the introduction of metal diaphragms inside the glass cross would lead to the presence of undesirable impurities especially when organic vapours at higher temperatures were being studied, the expedient of a double bulb was adopted, the constriction between the bulbs serving as a sort

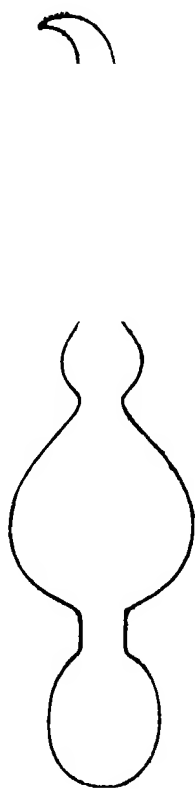


Fig. 1.

<sup>1</sup> The measurements on phenol and the following aromatic compounds were made with bulbs of smaller diameter (about 4 cm.)

of diaphragm, another diaphragm being provided by the slit in the black paint at the bottom of the smaller bulb.

The tube was mounted horizontally inside a thick iron cross tube so that the bigger bulb was at its centre. The cross was thoroughly blackened inside and provided with suitable diaphragms for shutting out stray light and arrangements were made for heating the cross electrically. The background end of the cross tube was closed by a blackened metal cap and the other ends were provided with glass windows.

Sunlight was concentrated by means of a lens at the centre of the bigger bulb and the polarisation in a direction perpendicular to the incident beam was measured in the usual manner with a double image prism and square-ended nicol. The maximum deviation of the incident rays from the axis was not more than  $3^\circ$  or  $1^\circ$  and no correction was made for this deviation. The temperature of the cross was usually kept not far from the boiling point of the substance. The following table gives the values of the depolarisation of the transversely scattered light for the substances studied.

TABLE I.

Substance	Temperature			Intensity of weak com- ponent ————— $\times 100$
				Intensity of strong com- ponent
Carbon disulphide ..	$40^\circ\text{C}$	14.3		16.7 (Ganesan) 12.0 (Raman and Rao).
Hexane	$60^\circ$	2.1		3.3 (Ganesan) 1.5 (Cabannes and Gauzit).
Cyclo-hexane	$60^\circ$	1.0		

TABLE I—*contd.*

Substance	Temperature	Intensity of weak component — $\times 10$ — Intensity of strong component	
Benzene	60°C	6.6	6.6 (Ganesan) 6.8 (Raman and Rao)
Phenol	205°	6.1	
Nitro-benzene	,	5.6	
Aniline	„	4.9	
Benzoic Acid	,	5.3	
Salicylic Acid	„	5.3	
Naphthalene	250°	7.9	
Ethyl Bromide	90°	3.2	
Ethylone Bromide	110°	6.7	

The results of measurements by previous investigators are given in column 4.

### *Discussion.*

It will be noticed that the values of the depolarisation for the single-ring aromatic compounds show significant variations among themselves. Aniline has thus a distinctly lower value than benzene showing that the substitution of H by  $\text{NH}_2$  reduces the optical anisotropy, which can be explained if the polarisation of the  $\text{NH}_2$  group is greater when the incident field is perpendicular to the "plane" of the benzene ring than when it is parallel to it. The same is true of the  $\text{COOH}$  group in benzoic and salicylic acids. Sir W. H. Bragg's analysis of the structure of benzoic acid crystals shows that the  $\text{COOH}$  groups of two neighbouring layers of molecules are turned towards each other and lie across the plane of

cleavage. Ganesan has found that the values of the depolarisation for chloro- and bromo-benzene are each  $\cdot 078$ , thus higher than that of benzene. This is just what we should expect in view of the larger refractivities of chlorine and bromine atoms. Naphthalene again has a larger anisotropy than benzene which is in consonance with its double-ring structure with two benzene rings placed side by side. The compounds ethyl bromide and ethylene bromide with ethane and ethyl alcohol form an interesting series. The values of depolarisation are as follow .—

Ethane	.	$\cdot 016$	Cabannes and Gauzit.
Ethyl alcohol	..	$\cdot 017$	Ganesan.
Ethyl Bromide	...	$\cdot 032$	} Table I.
Ethylene Bromide	.	$\cdot 067$	

The substitution of H or OH by the highly refracting bromine atom at the end of the molecule increases the influence of the polarisation of this atom on the other atoms and thus increases the anisotropy. If both the end atoms are replaced by bromine, the effect is accentuated. Krishnan <sup>1</sup> has obtained the same general variations with these substances in the liquid condition and also found that the corresponding chlorides show the same effect but to a smaller degree than the bromides.

#### *Experimental Results of Cabannes and his Co-workers.*

One disconcerting feature about the measurements of the depolarisation of light scattered by gases and vapours is the uniformly lower values obtained by Cabannes and his co-workers. The French investigators used a glass cross for their work and took great care in purifying their material. They think that the higher values obtained by other workers may be due to the presence of a trace of some impurity perhaps given out by the black paint used for blackening the insides of the metal crosses. From our experience, we are

<sup>1</sup> Phil Mag, Vol L, p. 697 (1925).

inclined to consider it possible that the lower values obtained by Cabannes and his co-workers may have been due to an imperfect background. The inside diameter of their glass crosses was three centimeters and no diaphragms were used for shutting out stray light. It might be thought that an unpolarised background illumination would affect both the components alike and would thus be of little importance, but it is not so. When we adjust the nicol so as to secure equality of brightness of the two tracks produced by the double image prism, its position is such as to cut off most of the illumination in the background of the brighter component and to transmit a considerable part of the illumination in that of the weaker component. The contrast between the track and its background is thus greater in the former case than in the latter, and our tendency either when viewing the tracks visually or when judging the density of photographic images is to overestimate the brightness of the track with the darker background; or in other words, when we think that the two tracks have been adjusted to be of equal brightness, the primary component is really weaker and the estimated value of the depolarisation smaller. For the same background illumination, the percentage error would be greater, the weaker the depolarisation of the scattered light. However, the possibility of the admixture of a small quantity of foreign matter is one to be kept in mind. It would be worth while to obtain careful measurements for a few substances having small values of depolarisation using a glass cross of larger dimensions than that used by Cabannes and his co-workers and provided with proper apertures for shutting out stray light.

#### *Optical Anisotropy of the Carbon Atom.*

Ganesan's measurement on the depolarisation of the light scattered by  $\text{CCl}_4$  vapour ( $\cdot 019$ ), Krishnan's measurement on  $\text{CCl}_4$  liquid ( $\cdot 061$ ) and Cabannes and Gauzit's on  $\text{CH}_4$  gas

(015) show definitely that we must assume a certain anisotropy of structure even in these molecules and since the four atoms attached to the central carbon atom are identical, an anisotropy of the carbon atom itself. Cabannes and Gauzit have discussed this point in their paper with reference to  $\text{CH}_4$  and they conclude that the carbon atom cannot possess regular tetrahedral symmetry. In this connection, it may be pointed out that according to Bohr's theory, the four outer electrons of the carbon atom, although they would possess considerable symmetry, cannot possess perfectly regular tetrahedral symmetry as their orbits are partly determined by the presence of the two internal electrons describing circular orbits whose planes are at an angle of  $120^\circ$  with each other. The anisotropy of the internal orbits must be reflected in the orbits of the outer electrons and the latter cannot therefore possess *perfect* symmetry. An extension of the argument shows that we must expect a certain amount of anisotropy even in the atoms of the inert gases, and the anisotropy of helium should be particularly marked. The only measurement of the depolarisation of this gas is that made by Lord Rayleigh who fixed an upper limit to its value at 6.5 per cent. An exact measurement of the depolarisation of helium is very much to be desired.

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## Note on Anomalies in frictional electricity.

BY

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It is generally believed that rubbing of two different substances is essential for producing electric charges. The one which occupies a higher position in the electric tension series is positive with one next to it. This general statement has exceptions as Faraday found that one part of a catskin is very negative to another part and even to rock crystal which is much lower in the series. He also found that different pieces of flannel differed very much from each other.<sup>1</sup> Something similar to this was observed with white and black silk ribbons.<sup>2</sup>

The mode of rubbing is a factor of considerably great influence in the production of what are called anomalous electric effects. Faraday was aware of this. He found that a feather struck lightly against dry canvas became strongly negative. Yet the same feather when drawn with a little pressure between the folds of the same canvas became strongly positive. It was further found that by altering the degree of friction any definite state could be put upon the feather. This point does not appear to have been further investigated with other substances till the year 1924, when T. Banfield and A. O. Rankine observed similar effects with Government

flannel and rough and smooth ebonite rods.<sup>3</sup> An effect akin to this was still more recently observed by Herbert Jones with a metal rod rubbed for a prolonged period with silk, the former undergoing fluctuations of potential.<sup>4</sup> Probably the most interesting feature of these 'anomalous' electrical effects is the rubbing of two similar pieces obtained by cutting into two a single piece. "When a piece of flannel is halved and the two pieces are drawn across each other, the two pieces will have different states irregularly, or the same piece will have both states in different parts, or sometimes both pieces will be negative, in which case, doubtless, air must have been rendered positive and then dissipated."<sup>1</sup> A. O. Rankine's observations in this connection with smooth and rough ebonite rods are rather interesting since they tend to show a certain constancy of electrical state—the unpolished rod always becoming positive and the polished one always negative. The effect of prolonged rubbing of two pieces of the same substance will be considered to be more interesting and I give below my observations for a few substances.

Two rods and disks were made out of a single piece of ebonite. The electrical effect of rubbing was detected by a Dolezalek electrometer of a sensibility of 88 mm/volt. During the process of prolonged rubbing it was found that a definite portion of each piece changed its electrical state so that at a particular time both of them may be positive or negative or one positive and the other negative, the charge on each being alternately positive and negative. The electrical state depended simply upon the amount of rubbing and appeared to be independent of the polish of the surfaces. The rubbing was continued to such a degree that the temperature of the ebonite pieces was considerably raised as was evident from the copious smell of caoutchouc coming out. It is also noteworthy that the charge was not symmetrically distributed in magnitude and sign over the



surface of one single piece. The following table gives the results for ebonite as well as for a few more substances.

Substance	Charge	Effect of prolonged rubbing
Ebonite } and Ebonite }	Both pieces either ( + ) or ( - ) or one ( + ) the other ( - )	Frequent reversals of electric state of each piece
India rubber (Grey)	One ( + ) the other ( - )	Reversals of state of each Ten- dency to constancy after very prolonged rubbing
India-rubber (Red)	Do	Do.
Sulphur from market	Both pieces ( + )	No reversals of state
Sulphur } and Rubber }	Sulphur + Rubber -	No reversals
Ebonite } and Rubber }	Ebonite - Rubber +	..
Charcoal	Both +	No reversals
Rock salt from market	Do.	Do
Pieces of candle	Each -	

It is difficult to say exactly why the reversals noted above occur. Probably in the case of ebonite which is a mixture of sulphur and caoutchouc the following process takes place : the two pieces are rubbed away in layers ; so that sometime a layer rich in sulphur particles rubs against a similar layer on the other piece or against a layer rich in caoutchouc. Similarly a layer rich in caoutchouc may rub against a similar layer on the other piece. It is, then, simply a case of rubbing sulphur against sulphur or sulphur against caoutchouc or caoutchouc against caoutchouc. The state of sulphur or caoutchouc in ebonite is not definitely known. Consequently it is difficult to determine the state of electrical charge. Probably a similar process takes place in other substances which are non-homogeneous. From the table it will be seen that sometimes the two pieces rubbed both show the same sign. In

this case obviously the opposite charge must go to air, the charge residing either on the molecules of air or on very small particles coming out of the pieces that are rubbed. Sufficient experimental evidence in this connection is necessary to confirm the mode of carriage of charge in air.

The study of frictional electricity is at its experimental stage and it would probably be too premature to put forward any view about development of electricity by friction. However it cannot be gainsaid that whatever may be the view it must be consistent with the present ideas of electric charge : the positive and negative charges are respectively the result of deficiency and excess of electrons. We are thus induced to hold the view that the process of electricity development by friction involves the emission and absorption of electrons. During rubbing considerable rise in temperature occurs. This was specially noticeable with ebonite, rubber and sulphur. Jones has actually measured the temperature in some cases and has found a definite relationship between the temperature and the potential of the substance.<sup>4</sup> It thus appears that thermionics play an important part in frictional electricity.

*Summary—*

(1) Anomalous frictional effects are known since the time of Faraday.

(2) Rankine's observation about rough and smooth ebonite rods appears to depart from accuracy when the rubbing is prolonged. The ebonite pieces show reversals of sign.

(3) A few more substances are observed. Of these India-rubber of red and grey variety show similar reversals.

(4) From the considerable rise in temperature of the rubbing substances and from Jones' observation about definite

relationship between the potential and the temperature of the substance it appears that thermionics play a considerable part in frictional electricity.

(5) The reversals in ebonite and rubber may be due to the non-homogeneous nature of these substances.

<sup>1</sup> Faraday Researches, Vol 11, p 125

<sup>2</sup> Nature Aug 2, 1924, p 152

<sup>3</sup> Proc. Phys Soc. London, 1924, Aug. 15, p. 430

<sup>4</sup> Phil. Mag, Nov 1925, p 1176

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## On the Methodology of studying the Slow Transformations of Solids.

BY

BORIS WEINBERG.

From 1903 to 1915 when the War had practically cleared up the student-population of the laboratories, I and my co-workers had been experimenting much on slow transformations of solids and very viscous liquids. Under this name I understand not only the changes of form under the action of forces exceeding the limit of elasticity but also the changes of the forces exerted by the solids when their deformation is kept constant. These researches were carried on mostly in the physical laboratories of the Odessa University and of the Tomsk Technological Institute, and also in the physical laboratories of the Petrograd and Göttingen Universities, and in the mechanical laboratories of the Petrograd Institutes of Ways of Communication, Electrotechnical, Technological and Polytechnical as well as in expeditionary (on the ice of Tyrol glaciers) and home (on the ice of Neva) conditions.

The last years this work was renewed—although more in the theoretical direction—but was again retarded by my removal from Tomsk to Leningrad. I would like therefore to summarise now the results of these investigations which are the subject of 52 papers. A part of the papers compiled during the last years is not yet published owing to the difficulties of printing which existed then. (For a list of the papers, see Bibliography at the end.)

(The quotations will be made in the following by indicating the number of the article in this list with the pages added)

In order to resume most succinctly the contents of the 700 pages of those papers we shall treat apart the methodology and the results and shall separately expose the researches concerning the laminar motion of typical viscous liquids

This paper being devoted to the first question—the methodology—we shall firstly try to answer what problems can be set before an investigator of transformations of a “solid” body subjected to forces exceeding its limit of elasticity and in what form the results may be represented.

When we are in search of the laws of a physical phenomenon we may generally meet three essentially different cases (17) :

A. All the quantities between which we intend to find the correlations can be simultaneously kept constant and are actually constant in each separate experiment.

B. All the studied quantities can be kept constant simultaneously but we must vary some or all of them during every experiment.

C. We cannot keep constant simultaneously all the quantities between which we are seeking the correlations.

In the first case the corresponding values  $x, y, z, \dots$  of the different physical quantities  $x, y, z, \dots$  which characterize the studied phenomenon can be represented :<sup>1</sup>

(a) Arithmetically—by a table or a series of tables (simple or of double entrance) giving the values of the variable quantity  $x$  (varying only from one experiment to the other) corresponding to definite values of  $y$  if  $x$  depends only upon  $y$  or upon different definite sets of the values of the variable quantities  $y, z, \dots$  if their total number exceeds two ;

<sup>1</sup> Cf. Boris Weinberg—On the Methodology of finding and representing the Distribution of a Natural Element over a certain Region of the Earth's Surface with Special Reference to Terrestrial Magnetism—*Teis. Magn.* 27. 137-155, 1924.

(b) Analytically—by one or several finite equations

$$\left. \begin{array}{llll} F_1 (x, y, z, \dots & \dots & \dots) = 0 \\ F_2 (x, y, z, \dots & \dots & \dots) = 0 \\ \dots & \dots & \dots \end{array} \right\} \quad (1)$$

(c) Geometrically.

If the number of variables is two (Boyle's law; the dependence between a constant potential difference and the current intensity; etc.) the geometrical image is a plane curve. The number of the variables being three (Van der Waal's formula; the boiling point of a solution, its concentration and the pressure; etc.) the image is a surface or a set of plane curves. If the number of the variables is four we can, if we like, represent their correlation by a set of surfaces.

In the case *B* the correlation of the quantities  $x, y, z, \dots$  can also be represented arithmetically by sets of tables containing the consecutive simultaneous values of the variables  $x, y, z, \dots$  in each single experiment and necessarily the values of the *time* when these values have been observed.

Such a representation being too complicated we are still more anxious than in the case *A* to find an analytical expression of the correlation which in this case can be only of the form of one or several *differential* equations connecting the values of the variables and of their differential quotients relatively to time.

$$\left. \begin{array}{llll} F_1 (x, y, z, \dots & \dots & \frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt} \dots \frac{d^2x}{dt^2}, \frac{d^2y}{dt^2}, \frac{d^2z}{dt^2}, \dots) = 0 \\ F_2 ( \dots & \dots & \dots & \dots & \dots & \dots) = 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \end{array} \right\} \quad (2)$$

If we would like to deal only with finite equations we ought to introduce as an independent variable the time but the problem would become indeterminate.

In order to show what kind of indetermination would be introduced let us fix the ideas and consider the simplest use of two variables  $x$  and  $y$ , *e.g.*, intensity of current and potential difference for which we have

$$IR = v - L \frac{dl}{dt}, \quad (3)$$

displacement of a material point and the force for which we have

$$m \frac{d^2 x}{dt^2} = X, \quad (4)$$

and so on. We can vary with the time one of the variables according to a definite regime

$$x = X(t) \quad (5)$$

which we choose at our will and then the other variable shall necessarily vary with the time in a quite definite manner

$$y = \psi(t) \quad (6)$$

If we eliminate  $t$  we obtain a finite equation connecting the variables  $x$  and  $y$

$$\phi(x, y) = 0 \quad (7)$$

but this equation is indeterminate, the form of the function  $\phi$  depending on the form of the function  $x$  which is at our disposal.

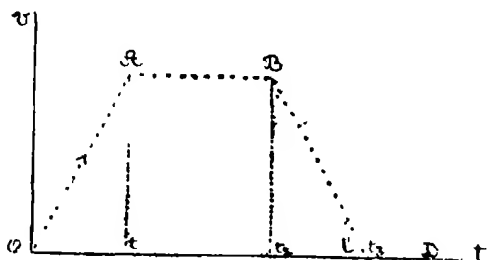


Fig. 1.

If we refer to geometric images the course of the phenomenon may be represented by two plane curves or by one curve in the space of three dimensions.

Let us for instance consider the case (30, 98-106) of I and V and increase V linearly with the time from the moment  $t=0$  to  $t=t_1$ , then keep V constant during an interval  $t_2=t_1$  and finally diminish V from  $t=t_2$  to  $t=t_3$  with the same celerity as during the first period until it becomes equal to zero as is indicated by the curve OABCD of Fig. 1. The intensity of current shall vary during the first period according to the law

$$I = \frac{aL}{R} - \left(1 - e^{-\frac{R}{L}t}\right) \frac{aL}{R^2} \quad (8)$$

if we denote  $\frac{aV}{dt}$  by  $a$ ; shall attain asymptotically the value  $\frac{aL}{R}$  in the second period; and so on. These variations may be represented by the curve  $O\alpha\beta\gamma\delta$  of Fig. 2. The function  $\phi$  (F) connecting the simultaneous values of I and V shall be given by the curve  $O a b c O$  (Fig. 3) and the whole phenomenon may be also represented by a single geometric image—one curve in the space of three dimensions

The stereoscopic photographs of a model reproducing this curve are given by Fig. 4. The axis of I is directed upwards, the axis of V—to the right and the axis of the time  $t$ —backwards. The metallic wire stained in white represents the curve in the space; its projection on the plane  $Vt$  is reproduced by a wire stained in large pieces alternately white and black so that we obtain the dotting;

— — — — —  
its projection on the plane  $Vt$  is dotted

— — — — —  
and its projection on the plane  $Tv$  is dotted

.....  
The essential feature of all such curves is that they are *unicursal*, i.e., that they can be traced by the representative



point only in *one* completely definite direction—the direction which corresponds to the *increasing* values of  $t$ .

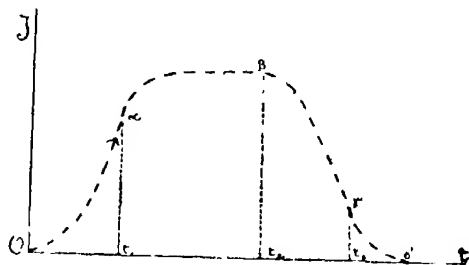


Fig. 2.

If the differential law or laws connecting the variables and their differential quotients is unknown we have to study experimentally different cases of the correlated functions (5) and (6) (if the number of the variables is equal to 2) by assigning to one or several of the variables definite regimes and by observing the concomitant variations of the remaining variable. A collection of such pairs of the curves  $X$  and  $Y$  can by induction lead the investigator to the differential equations of the type (2).

The problem is still more complicated in the case  $C$  when the constancy of all the variables cannot then be attained simultaneously. Let us confine to two variables, as for instance: the force acting on a solid and exceeding its limit of elasticity and the deformation; the temperature indicated by a liquid thermometer and its *true* temperature; the moment of a "constant" magnet and its temperature; the magnetic induction of a ferromagnetic body and the intensity of the magnetic field; etc.

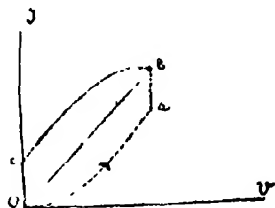


Fig. 3.

This third category of the natural phenomena—perhaps the most numerous and the most general—is very similar to the second: we must prescribe to one of the variables a definite regime—*e.g.*,  $x=x(t)$ —and observe the simultaneous values of the other variable. The only difference—quite essential from the physical standpoint—is that if we keep constant—so to say “by force”—one of the variables the other continues to change independently and we are powerless to maintain its unvariability. From the mathematical standpoint this difference seems to make impossible the reproduction of the correlation between the variables by a differential equation of the type (2) but only by an equation in partial differentials.<sup>1</sup>

$$x(x, y, t) dx + \psi(x, y, t) dy + \tau(x, y, t) dt = 0 \quad (9)$$

These general considerations show clearly the necessity of studying definite *regimes* for the categories *B* and *C* of the natural phenomena and in particular for the transformations of the solids subjected or having been subjected to forces exceeding the limit of elasticity.<sup>2</sup>

Indeed if we keep constant the deformation  $x$  the force  $f$  diminishes spontaneously with the time and we have before

<sup>1</sup> Cf. Brillouin, Journ. de phys. 7, p. 330, 1888.

<sup>2</sup> Without insisting on the lack of precision in the usual definitions of this notion (30, 81-82) I would like to call attention to the investigations of G. V. Trapeznikov (Trans. of the III Meet. of the Russ. Ass. of Phys., 25-26, 1923, and further publications in the Bull. of the Tomsk Techn. Inst.) This author has shown that the limit of elasticity has a quite definite value if we define it as the abscissa OK (Fig. 5 relating to compression) corresponding to the intersection of two lines representing the length of a sample after a short application of gradually increasing forces: the first line is the straight line AB parallel to the axis of forces and passing into a concave section BC when the so-called limit of elasticity is reached, and its prolongation to the right and the second line is the convex line CD representing the residual lengths after the limit of elasticity is considerably exceeded, and its prolongation to the left. The part BC is different for different samples whilst the abscissa OK shows a considerable constancy and is equal to twice the analogous “theoretical limit of elasticity” for extension and to 1/750 of the Young’s modulus for all the metals which have been investigated.

us the phenomenon of relaxation for which different authors have proposed, on account of theoretical considerations or of experimental investigations, various formulæ. Here are some of those :

$$\text{Maxwell}^1) f = f_0 e^{-\frac{t}{J}}, \quad \frac{df}{dt} = -\frac{f}{J} \quad \left. \vphantom{\frac{df}{dt}} \right\} \quad (10),$$

( $J$ —the “ time of relaxation ”).

$$\text{Schwedoff}^2) f - \delta = (f_0 - \delta) e^{-\frac{t}{J}}, \quad \frac{df}{dt} = -\frac{f - \delta}{J} \quad \left. \vphantom{\frac{df}{dt}} \right\} \quad (11),$$

( $\delta$ —the limit of elasticity),

$$\text{Bonasse}^3) \left\{ \begin{array}{ll} \text{“ déperdition rapide ”} & f = f_0 - a e^{-ht} \quad \dots (12), \\ \text{“ déperdition lente ”} & f = f_0 - a \lg \frac{t + \tau}{\tau} \quad \dots (13), \end{array} \right.$$

$$\left\{ \begin{array}{ll} f = f_0 - a \lg (t + 1) & \dots (14), \end{array} \right.$$

$$\text{Trouton and Rankine}^4) \left\{ \begin{array}{ll} f = f_0 - a \lg t & \dots (15), \end{array} \right.$$

$$\left\{ \begin{array}{ll} f = f_0 - a \lg \frac{1 + pt}{1 + qt} & (16) \end{array} \right.$$

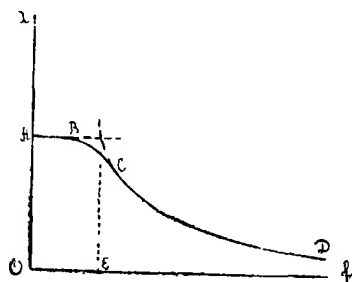


Fig. 5.

The explanation of other regimes of a solid must be intimately related (12, 34) to our notions of its structure as

<sup>1</sup> Phil Trans 157, p 49, 1868, or Phil Mag. 35, p 129 and p 185, 1868

<sup>2</sup> Journ de phys. 8, p. 34, 1889, 9, p 34, 1900

<sup>3</sup> Ann Fac Toulouse 2, p 458, 1900

<sup>4</sup> Phil Mag 8, p. 538, 1904.

of an assemblage of separate, "crystallites"—according to the terminology of *Tammann*—surrounded by very thin layers of amorphous (or rather eutectic?) solder and to the possible forms of the residual deformations of these crystallites and the relative motions of each of them relatively to the neighbouring ones as a whole. But the explanation of the phenomenon of relaxation as well as of the variations of the limit of elasticity suggested by the variations of the maximal strain to which the solid was subjected and by the time itself must be connected to the phenomenon of "recrystallisation" to which such attention is duly paid now by *Tammann* and his co-workers and by other investigators.

I would like to mention the necessity of the investigations also on the phenomenon of *reconstitution* which may be considered as opposite to the relaxation and consists for instance in a gradual growing together or a coalescence of the parts of a body when they were previously separated from each other and then pressed together.

If on the other hand the force is kept constant it is the deformation which is continuously increasing although the question whether for a typical solid (metals, crystals) the deformation  $x$  itself or its differential co-efficient relatively to time  $\frac{dx}{dt}$  is tending asymptotically to a definite limit is still not quite definitely answered notwithstanding experiments lasting many months (40 & 41). Attempts to include this phenomenon in the form of a mathematical formula were made by *Bouasse*,<sup>1</sup> *Philipps*,<sup>2</sup> *Andrade*,<sup>3</sup> and *Mallock* & *Ritter*.<sup>5</sup>

Ann. chim. phys. 2, p. 479, 1897, Ann. Fac. Toulonae 1, 361, 1899

Phil. Mag. 9, p. 513, 1905.

Proc. R. Soc. Lond. 84A, p. 1, 1911.

Proc. R. Soc. Lond. 95A, p. 420, 1919

Phys. Zts. 22, p. 53, 1921.

$$Bouasse \quad . \quad x = a \lg (bt + 1) \quad . \quad \dots \quad (17),$$

$$Philippus \quad x = a + \lg, t \quad \dots \quad (18),$$

$$Andrade \quad . \quad x = a \left[ (1 + bt)^{\frac{1}{3}} e^{kt} - 1 \right] \quad \dots \quad (19),$$

$$Mallock \quad \dots \quad x = a \left( 1 - e^{-kt} \right) \quad . \quad \dots \quad (20),$$

$$Ritter \quad \dots \quad x = a \lg t \quad . \quad \dots \quad (21),$$

A great number of researches were devoted to the particular case  $f=0$ , i e., where the force after having exceeded the elasticity and acted for a certain interval of time is kept limit of equal to zero—to the phenomenon of the so-called “elastic after-effect” (“elastische Nachwirkung”). In order not to lengthen unduly this article I shall not quote the numerous formulae which have been proposed and are from time to time continued to be proposed for explaining this phenomenon and shall only mention that they must be of the type.

$$x = \phi(f_0, t + \tau) + \phi(-f_0, t) \quad .. \quad \dots \quad (22)$$

where  $f_0$  is the force to which the solid has been previously subjected during the interval of time  $\tau$  and  $\phi$  is a function analogous to (17)—(19).

For finding the equation (10) or a similar generalisation of the laws governing different regimes we ought to study not only the mentioned simplest regimes  $x = \text{const.}$ ,  $f = \text{const.}$ ,  $f = 0$ <sup>1</sup> but also various other regimes. The only condition is that these regimes should be quite definite as so eloquently emphasised by *Bouasse* in pointing out the necessity of scrupulously avoiding the most insignificant uncertainty of these regimes.<sup>2</sup>

If even we limit ourselves by the simplest cases—of linear changes with the time—the variety is quite considerable

<sup>1</sup> It would be also interesting to study the regime  $x=0$  the variations of the force when the deformation is kept equal to zero after the sample has suffered a deformation under the action of a force exceeding the limit of elasticity.

<sup>2</sup> See e.g., *Ann. Fac. Toulouse* 3 (2), 213—221, 1901.

as may be seen from the model the stereoscopic photographs of which are given by the Fig. 6. This model represents only the cases of the constancy or of the linear changes with the time  $t$  (the axis of  $t$  is directed backwards) of the force  $f$  (the axis of  $f$  is directed to the right) or of the deformation  $x$  (the axis of  $x$  is directed upwards).

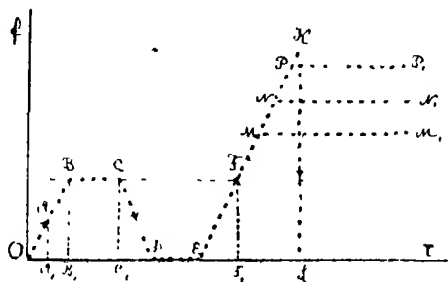


Fig. 7.

Let us increase the force linearly—the section  $OAB$  of the Fig. 7—so as to surpass the limit of elasticity  $AA_1$  and let us then successively maintain the force constant and equal to  $BB_1$ , diminish it linearly—section  $CD$ —, keep it during a certain time equal to zero— $DE$ —, again increase it linearly— $EK$ —, until the body attains its “limit of plasticity” (the “tensile strength”) and breaks or until we stop this increase of the force at some definite smaller value— $MM_1$ ,  $NN_1$ ,  $PP_1$ .

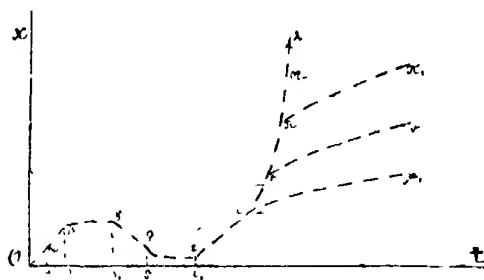


Fig. 8.

On the model these forced variations of the force are reproduced by the wire dotted.....and situated in the upper horizontal plane and also in the lower one. The corresponding variations of the deformations are represented on the Fig. 8 by the sections  $Oa$  (*Hooke's* law),  $\alpha\beta$ ,  $\beta\delta$ ,  $\delta\delta$ ,  $\delta\epsilon$  (elastic after-effect),  $\epsilon\iota$ ,  $\iota x\lambda$  with the lateral branches  $\mu\mu_1$ ,  $\nu\nu_1$ ,  $\pi\pi_1$  and in the model (Fig. 6)—by the wire dotted — — — — —and situated in the plane  $xt$  (this wire has no correspondent in the plane to the right). The form of the three lateral branches which correspond to the three large values of a constant force is here based on the supposition that in such cases a constant celerity of deformation is attained and that this celerity is proportional to the excess of the force acting against the limit of elasticity—analogy to the formula (11).

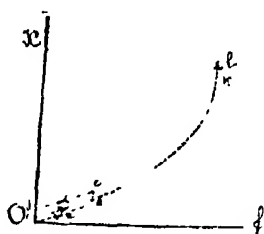


Fig. 9.

In a single geometric image these parallel variations of the force and of the deformation with the time are represented on the model (Fig. 6) by the white wire nearest to the observer. The projection of this curve on the plane  $fx$  which represents geometrically the simultaneous values of  $f$  and  $x$  is represented in the model by the corresponding wire dotted.....and situated in the front plane and separately—by the curve  $Oabdebkl$  of the Fig. 9.

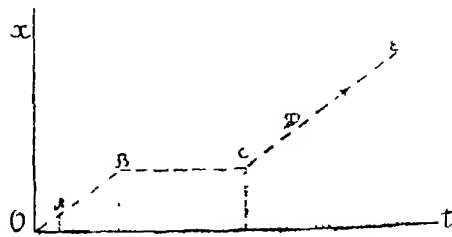


Fig. 10.

Let us take now a new sample of the same material identical to the first one and increase linearly the deformation—section OAB of the fig. 10—then keep it constant—BC—and finally increase it linearly until the limit of plasticity is reached. These variations are represented by the wire dotted— — and situated in the right (as well as in the left) plane of our model. The concomitant variations of the force are given in function of the time by the sections  $Oa\beta$ ,  $\beta\gamma$  (relaxation)  $\gamma\delta\epsilon \in L$ , of the fig. 11 and by the wire dotted .. .. and situated in the lower horizontal plane  $ft$  of the model. In function of the deformation they are given by the curve  $Oa_1 b_1 c_1 d_1 e_1 l_1$  of the fig. 12 and by the wire dotted ... .. and situated in the front plane  $fx$  of the model. All these curves are also *unicursal*

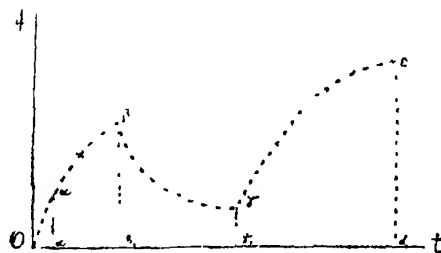


Fig. 11.

It may be added that if a body obeys the law of relaxation of *Marwell* or of *Schvedoff*—(10) or (11)—respectively and if we deal with simple shear of unit area



and denote by  $N$  the modulus of rigidity, by  $\alpha'$ —the angle of shear and by  $\alpha'$ —the angular velocity of shear, the constant value of  $\alpha'$  shall produce the increase of force according to one of the formulae (30, 108)

$$f = f_0 e^{-\frac{t}{\tau}} + N\tau\alpha' \left(1 - e^{-\frac{t}{\tau}}\right) \quad \dots \quad (23),$$

$$f = f_0 e^{-\frac{t}{\tau}} + \left(N\tau\alpha' + \delta\right) \left(1 - e^{-\frac{t}{\tau}}\right) \quad \dots \quad (24),$$

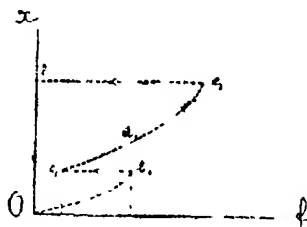


Fig. 12

These formulae give for  $t = \infty$  the following values of the coefficient of internal friction  $\eta$  respectively.

$$\eta = \frac{f}{\alpha'} = N\tau \quad \dots \quad (25),$$

$$\eta = \frac{f}{\alpha'} = N\tau + \frac{\delta}{\alpha'} \quad \dots \quad (26),$$

Beside the regimes of constancy or of linear variations of one of the two variables, force and deformation, only the periodic regimes when we have cyclic changes of different types, have been the subject of numerous investigations, without, however, leading to results which could be considered as sufficiently conclusive and general.

<sup>1</sup> Their enumeration—till 1905 and 1912 respectively—may be found in my articles 3 (218) and 30 (98).

I am of the opinion that these periodic transformations are less liable to contribute much to the physics of solids than the more steady and *slow* transformations.

Indeed when we pass through the gate of the Limit of Elasticity and enter into the domain of mysterious and omnipotent Chronos, the time itself affects the value of the force or of the deformation—beside the value which we by our will are imposing to the other variable. This influence of the time is more marked and also more irregular the first minutes and hours than during the following. Therefore the periodic transformations, in which the solid has too little time to adapt itself to the double influence of the force or the deformation and of the time, must be more difficult for interpretation than the slow and steady transformations.

But the study of slow deformations offers also great difficulties because we must give to the time enough time to exert fully its influence—several weeks, months and even years for typical solids (metals, crystals). The more the solid resembles a liquid, the lower is its limit of elasticity and its co-efficient of internal friction—the more this interval of time may be diminished and the celerity of deformation augmented.

Another difficulty is that we cannot *repeat* an experiment on a solid beyond the limit of elasticity and that we must *renew* the experiment with a new identical sample irreparable tempus “ makes irreparable every solid and to make two or more identical samples from a solid material is incomparably more difficult than to take two identical portions of a liquid.

Let us pass now to the question from what kind of deformations we can hope to extract the most fruitful results. Each deformation being decomposable into the change of the volume and the change of the form (uniform or non-uniform shear) it seems preferable to study at first the deformations

in which we have only the changes of the volume or only the changes of the form. Corresponding to the diminution of the volume there does not probably exist a limit of elasticity and decidedly there does not exist a limit of plasticity. Concerning the increase of volume we may doubt the existence of the limit of elasticity but affirm with certitude the existence of the limit of plasticity although the experiments on omnilateral extension are almost impossible—if we do not deal with a typical liquid—and are not yet performed and even attempted. Therefore we must preferably chose such kinds of deformation where we have only the change of the form.

But beside the greater probable simplicity of the results of studying such deformations there are some complementary conditions which the method of studying must fulfil in order that this study would be advantageous. These complementary conditions are :

1. Uniformity of the deformation,
2. Possibility of measuring the deformation with sufficient precision and sensibility,
3. Possibility of continuing the experiment sufficiently long.

How important these qualities are may be seen from the example of the deformation of unilateral extension (accompanied by the transversal contraction) which fulfils all the three conditions and has therefore been the favourite object of numerous and various researches.

I would like to mention here but one of those—namely of E. A. *Kirillov* (10 & 11) who studied the extension of a long (18m) steel wire under the action of small (2kg) overcharges added to a variable fundamental weight. He found the constancy of  $E$  within 0.5% for elongations  $\Delta l/l$  amounting to 0.004 whilst J. P. Thompson<sup>1</sup> has obtained

<sup>1</sup> Wied. Ann., 44 p. 555. 1891.

variations of  $E$  equal to 3·8% for  $\frac{\Delta l}{l}=0\cdot002$  and  $F. A.$

*Schultze*<sup>1</sup>—a variation of 4% for  $\frac{\Delta l}{l}=0\cdot010$ . But if we consider (30, 76—78) that *Thompson* was measuring the total elongation of a new wire under short action of gradually increasing weight and that *Schultze* was operating with small overcharges changing periodically (about 2200 times per second) their value and their sign and other peculiarities of these three investigations we cannot reject the deductive hypothesis of the exactitude of the *Hooke's* law—at least after a prolonged action of a big charge and for forces smaller than it.

Objecting to the unilateral extension the co-existence of the changes of the form and of the volume I have tried for my part to ameliorate and to multiply the methods of studying the deformations not accompanied by the change of the volume. The last condition is fulfilled always if the exterior forces are volume forces or if they are surface forces but without normal components.

Let us enumerate now the different kinds of such deformations including in the list those which are applicable only to materials relatively soft.

I. *Simple or helicoidal Torsion* (proposed by *Coulomb*; used in a great number of researches). One of the bases of a cylinder or of a cylindrical tube—more seldom of a rectangular prism is turned around the axis of the cylinder relatively to the other; the radii of the sections perpendicular to the axis remain rectilinear and the generatrices are transformed into helices.

II. *Spiral form torsion* (*Couette*, *Schwedoff*—liquids; *Grübler*<sup>2</sup>—cement; *Weinberg* and *Smirnov*—19—pitch; *Weinberg*—21—pitch and asphalt). One of the lateral

<sup>1</sup> Ann d Phys. 31, p. 1 1910

<sup>2</sup> Zts. d. Ver. deutsch. Ing. 53, p 449., 1909.

surfaces of a cylindrical layer turns around the axis of the cylinder relatively to the other: the generatrices remain rectilinear and the radii of transversal sections are transformed into spirals.

III. *Shearing of a parallelopiped* (*Obermayer*<sup>1</sup> (probably also by *Nutting*<sup>2</sup>)—pitch; *Weinberg* and *Smirnov*—19—also; *Weinberg*—1, 40, 41 and 35—lead, Iceland spar, rock salt, clay; *Andrade*<sup>3</sup>—gelatine). One of the bases is subjected to a displacement parallel to the other one.

IV. *Shearing of two adjacent parallelopipeds* (proposed by *Weinberg*—19, applied by *Dudeckij*—29—to asphalt). The bases of two parallelopipeds made parallel and turned one towards the other are displaced parallel to their surface and relatively to two other bases which are kept fixed.

V. *Shearing of a Tore* (proposed by *Weinberg*—27; applied by *Dudeckij*—29—to asphalt). One of the bases of a tore of rectangular section turns around the axis of the tore relatively to the other.

VI. *Axial shearing of a cylindrical layer* (*Tammann*<sup>4</sup> relative measurement on supercooled liquids; *Segel*<sup>5</sup>—sealing wax; *Weinberg* and *Smirnov*—19—pitch; *Weinberg*—21—asphalts). The lateral interior surface of a cylindrical layer is displaced parallel to the axis and relatively to the lateral exterior surface.

VII. *Flow in a tube under the action of gravity* (*A. f. mov* and *Weinberg*—32—solutions of dammar in turpentine-oil; *Gostjunin* and *Le Denta*—22—pitch; several other researches—33, 36—made in the physical laboratory of the Tomsk Technological Institute). The lateral surface of a vertical cylinder of the substance is maintained fixed; the cylinder deforms under its proper weight

<sup>1</sup> Sitzber Wien Akad 75, p 665 1877, 113, IIa, p 511 1904

<sup>2</sup> Phys. Rev 18, p 107 1921

<sup>3</sup> Proc. R Soc Lond 85A, p. 448 1911

<sup>4</sup> Zts Phys Chem. 28, p 17 1899

<sup>5</sup> Phys. Zts 4, p 493 1903

VIII. *Flow in an inclined channel under the action of gravity* (*Weinberg*—2, 3, 5—the theory of glaciers and—13, 14, 15, 23—experiments on pitch). The bottom surface of a channel or gutter of a uniform section is maintained fixed and inclined to horizon; the substance filling the channel flows down from a reservoir placed at the upper extremity of the channel into another one placed at the lower extremity.

Most of these methods having been used especially for the determination of the co-efficient of internal friction of solids, I shall, for sake of completeness, indicate other methods used for the latter purpose although in those methods the changes of the form are accompanied by the changes of the volume.

IX. *Pressing through a tube* (*Barus* <sup>1</sup>—marine glue; *Heydweiller* <sup>2</sup>—menthol; *Reiger* <sup>3</sup> and *Glaser* <sup>4</sup>—mixtures of colophonium and turpentine-oil). The substance adhering to the walls of a tube is pressed through it by external pressure.

X. *Compression of a cylindrical disc* (*Obermayer* <sup>5</sup>—pitch; *Koch* <sup>6</sup>—ice). A cylindrical disc or a cylinder is compressed in the direction of its axis.

XI. *Longitudinal extension of a cylinder* (*Mc Connell and Kidd* <sup>7</sup>—ice; *Trouton* <sup>8</sup>—pitch, *Duntstan* <sup>9</sup>—tin). A cylinder is elongated parallel to the axis.

<sup>1</sup> Phil Mag 29, p 337 1890, Amer. Journ of Sc 15, p 87 1893.

<sup>2</sup> Wied. Ann. 63, p. 56. 1897.

<sup>3</sup> Ann. d. Phys 19, p. 985. 1906

<sup>4</sup> Ann. d Phys 22, p 694 1907

<sup>5</sup> Sitzber Wien Akad 75, p. 665 1877, more perfect theory is given by *Natanson*—Bull Acad. Crac 1902, p. 494.

Wied. Ann 25, p. 438 1885; or Ber naturw ges Freiburg 8, p 314 1885

Proc. R. Soc Lond 14, p 331 1888

Proc R. Soc. Lond. 77, p. 426 1900

Phil. Mag. 17, p. 192 1909.

XII. *Bending of a prism* (*Mc Connell* <sup>1</sup>—ice; *Hess* <sup>2</sup>—ice and tin; *Bond* <sup>3</sup>—ammonium nitrate). The ends of a prism are laid on two supports and its midst is charged by a weight.

XIII. *Pressing through on orifice*—many authors <sup>4</sup>. The substance filling a cylinder and not adhering or slightly adhering to its walls is expelled through an orifice in the bottom of the cylinder by pressure of a piston or of a liquid.

XIV. *Down motion through the substance of a sphere of another density* (*Tammann* <sup>5</sup>—relative measurement on over-cooled betol and piperin; *Trouton and Andrews* <sup>6</sup>—sealing wax). A sphere heavier than the substance is going down through it under the action of the apparent weight of the sphere.

XV. *Determination of the modulus of rigidity  $N$  and of the time of relaxation  $T$*  (*Reiger* <sup>7</sup>—different solutions of gelatine and colophonium). The value of  $N$  is determined by some of usual methods and of  $J$ —from the progressive diminution of the accidental double refraction caused by a compression; the value of  $N$  is calculated by means of the formula (22).

Different authors use—explicitly or implicitly three different definitions for the co-efficient of internal friction  $\eta$ :

1.  $\eta$  is the force relating to a unit of area and to a unit of angular velocity of shearing at the given moment of the deformation.

<sup>1</sup> Proc. R. Soc. Lond. 49, p. 323. 1891.

<sup>2</sup> Ann. d. Phys. 8, p. 405. 1902.

<sup>3</sup> Phil. Mag. 47, p. 1. 1921.

<sup>4</sup> The enumeration of such researches may be found at *Barus* (Bull. U.S. geol. Survey N71, 1891), *Spring* (Rapp. Congr. intern. de phys. 1, p. 402. 1900), *Obermayer* (Sitzber. Wien Akad. 113, II a, p. 511. 1904) and *Kurnakov and Jemcujuy* (Zts. Phys. Chem. 1913).

<sup>5</sup> Zts. phys. Chem. 28, p. 17. 1899.

<sup>6</sup> Proc. Phys. Soc. Lond. 19, p. 47. 1904 or Phil. Mag. 7, p. 347. 1904.

<sup>7</sup> Phys. Zts. 2, p. 213. 1901.

2.  $\eta$  is the same force but when the process of deformation has become stationary ;

3.  $\eta$  is the part of the latter force which depends on the celerity of deformation but not the deformation itself.

The second definition corresponds to *Maxwell's* law of relaxation—(10)—the third—to the *Schwedoff's*, if the angular velocity of shear becomes infinite. The first definition seems to be the most general, but in admitting it,  $N$  is no more a physical constant of the material. In order to avoid this uncertainty we must introduce the condition of stationariness.

From this standpoint the methods XIII and XIV are good only for materials which possess a sufficiently low limit of elasticity and for which the process becomes stationary very soon. In the opposite case the process is only *quasi* stationary because it is always new masses that are coming into play and are subjected to only the first stages of the whole process of their deformation. The interpretation of the observed phenomena must be rather complicated—still more complicated than even the interpretation of the cyclic torsions where at the limit of the limits, we observe really the preponderant influence of the last torsion on which is superposed the sum of the gradually extinguishing influences of all the previous oscillations.

For the usual metals—even for metals as soft as lead—the process does not become stationary even after many months as I was convinced by my observations of the torsion of a lead tube under the action of constant forces during 9 months (41) or of the increase of the moment of torsion of a long copper wire the other end of which has been turned with a constant angular velocity for more than two years (16). All



these circumstances suggest that the method of flow through an orifice and the notion of the "flow-pressure" which has given so many interesting physico-chemical results to *Kurnakov* and his co-workers<sup>1</sup> are less valuable from the purely physical standpoint—at least now when the phenomena of the deformation of solids are only beginning to be studied systematically and with the inclusion of the time in the number of the independent variables. The value of the "flow-pressure" which according to these researches is proportional to the "hardness" of the material (determined for instance by *Brinell's* method) can be confronted more properly with the limit of elasticity—inferior or superior<sup>2</sup>—than with the co-efficient of internal friction.

What concerns the method XV it must await a direct confirmation of the formula (26). For this purpose we must find a material which obeys *Schwedoff's* law and has at the same time a sufficiently high limit of elasticity to allow its direct measurement and the study of this material in its elastic stage. It may be presumed (5, 190) that besides feeble solutions of gelatine in water studied by *Schwedoff* and several other investigators, dried gelatine<sup>3</sup> and copal varnish<sup>4</sup> obey *Schwedoff's* law but the first material would not permit to study the plastic phase and the second—the elastic one. Ice (*Weinberg*, 3, 5, 6, 8) and asphalt (*Weinberg*—21; *Monstrov*—24 and 25; *Miloradov* and *Tolmacev*—26; *Dudeckij*—29) are more promising for the possibility of confirming equation (26).

<sup>1</sup> A summary of these researches is given for instance in the paper of *Kurnakov* and *Jemcujny* mentioned in the note 36

<sup>2</sup> See *G. Tammann*, *Gött. Nachr.*, 1911, p. 211 and *G. Tammann* and *O. Faust*, *Zts. Phys. Chem.* 75, p. 106, 1911.

<sup>3</sup> *Reiger* "Innere Reibung plastischer und fester Körper," *Inaug. Diss. Braunschweig*, Vieweg, 1901

<sup>4</sup> *G. de Metz* "La double refraction accidentelle," *Scientia*, N. 26, Paris *Gauthier-Villars*, 1901; *C. R.* 136, p. 604, 1903.

The methods IX—XII have not this defect: the deformation is stationary but the changes of volume can vitiate the results. If we assume *Poisson's* ratio  $\sigma$  to be equal to 0.5 the last objection is annihilated and for instance we obtain for the method X that the "co-efficient of the viscous traction" (*Trouton*, l. c.) is three times as great as the co-efficient of internal friction—a result which was confirmed by *Trouton* for pitch.

If the assumption  $\sigma=0.5$  is doubtful or decidedly wrong we must recur to one of the methods I—VIII. All these methods necessitate the use of materials which would be much more resistant than the substance we are studying and require that the adhesion of this substance to those materials should exceed the cohesion of the substance itself. The last condition has caused many troubles in our investigations on clay and the difficulties were overcome only by using the method III and by applying a pressure to the wooden plate adjacent to the upper base of a clay parallelopiped.

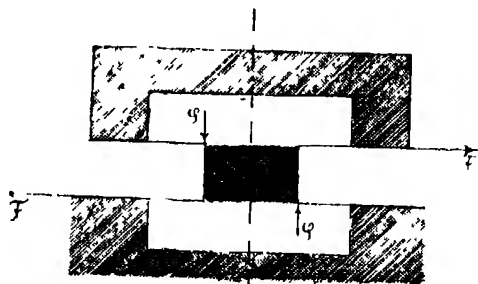


Fig. 13.

In general this difficulty plays in the methods I, III, IV and V—particularly in the method I—because you can if

necessary make at the extremities of the sample corresponding enlargements and use special settings. For the method III, I have given to the sample (lead) the form represented by the figs. 13 and 14 and for the method IV—by the fig. 15; the shaded parts indicate the parallelepipeds subjected to the shearing. In both cases we still have not a pure shear because besides the forces  $F$ ,  $F$  which produce this shear there are the forces  $\phi$ ,  $\phi$  of reaction of the enlarged parts which complicate the results. In the method V this defect is absent and therefore it can afford the greatest approximation to the uniform shear—especially if we give to the section of the tore to be twisted the form of the fig. 14: the relation of the angles of the torsion of the outer and of the inner layers of the tore being equal to the relation of their radii does not differ then practically from 1.

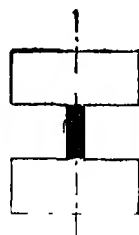


Fig. 14.

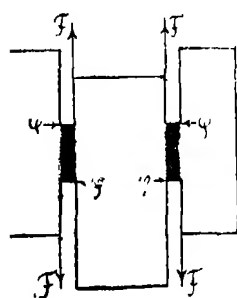


Fig. 15.

The methods VII and VIII have another practical inconvenience to give the possibility of applying only small forces—not exceeding the weight of the substance—and are therefore appropriate only to materials which have a minimal limit of elasticity and flow under the action of their own weight. In order to apply for such materials the methods I and III (if necessary also IV and V) we ought to use the immersion in a liquid of the same density but if  $\eta$  is not too small it suffices for the application of the method I to lay the cylinder to be twisted on a mercury bath (26).

The methods II and VI are more universal but the latter has the defect that the deformation cannot be increased indefinitely (as also in the methods III and IV). The process is regular during the initial stages (sufficiently long if the celerity of deformation is small) but this phase passes afterwards into another which is characterized by increase of the celerity (the force being unchanged) and by a sort of sliding along one of the surfaces of shear of some inner part of the cylinder as a whole (fig. 16). An analogous phenomenon I have observed by the method II the cylindrical layer dividing itself internally into two which were after that not only continuing to be deformed but were also sliding one relatively to the other.

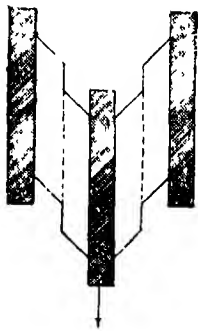


Fig. 16.



Fig. 17.

The methods II—VIII are not sufficiently sensible and therefore prohibit to study the process of deformation in all its details. On the contrary the method can afford practically illimitable sensibility and duration of the deformation but the deformation is ununiform and this circumstance embarrasses the interpretation of the results. This imperfection can be diminished by twisting a tube instead a cylinder but then is felt the inevitable inhomogeneity of the material itself and of the thickness of the walls of the tube : the more feeble parts in the longitudinal direction give finally rise to an exaggerated local twist (schematically represented by the fig. 17) and the inequalities in different parts of transversal sections produce finally local or longitudinal folds (fig. 18) rendering the continuation of the experiment useless.

We see thus there is no universal method for the study of slow deformations of solids and viscous liquids but the variety of the methods is sufficient to give the possibility in



Fig. 18.

every particular case to make a suitable choice which we would like to consider to be facilitated by the considerations elucidated here above.

These considerations have to be complemented by some indications on the practical realisation of the regimes  $f = \text{const.}$ ,  $f = 0$ ,  $\chi = \text{const.}$ ,  $\chi' = \text{const.}$  two of which— $f = \text{const.}$  and  $\chi' = \text{const.}$ —render possible the determination of  $\eta$  according to the 2—d and 3—d definitions of page 24.

To realise the regime  $f = \text{const.}$  the best expedient is to recur to the gravity because a force caused by a constant deformation of an elastic solid is always liable to suspicion on account of the not excluded possibility of the existence of the phenomenon of relaxation even below the limit of elasticity. But if a constant force is realised by the weight of a certain load it must act without the intervention of any pulleys and so on as well as the sample must be quite free to undergo the desired deformation. These desiderata are easy to be fulfilled for the methods IV and VI (for the methods VII and VIII they are fulfilled *eo ipso*) but in other cases we have to recur either to pulleys or to some bearings for the sample (for instance for the free end of the twisted cylinder in the method I if its axis is horizontal). In such cases the regime  $f = \text{const.}$  is fulfilled only approximately, the force in reality oscillating around a mean value on account of the forces of friction and of inertia (5, 300; 19, 14; 40, 43; 41, 30).

This circumstance became quite clear after the experiment of *A. V. Verhovskij* (Comm. Scient-Tech. res. 12, 10—11, 1924) who has investigated the deformations of two solids pressed to each other and exhibiting “dry” friction *before* we observe their relative motion. We found that this deformation amounting to  $2-3\omega$  in the direction of the subsequent motion—obeys the laws which govern the deformation of a solid subjected for instance to extension or bending: *Hooke's* law before attaining the limit of elasticity, greater deformations after the latter is exceeded, linear diminution of the deformation when the stress is taken off, with a resulting residual deformation, linear increase of the deformation when the stress is again laid on, if only it does not exceed the previous

maximum, and so forth. When the acting stress exceeded a certain value— a sort of the limit of plasticity— started the visible motion which was not uniform but proceeded by leaps of several  $\mu$ <sup>1</sup>.

Let us consider a weight acting in horizontal direction by means of a wire or a string and a pulley on a solid and exceeding its limit of elasticity. The solid yielding to this action must increase gradually its deformation so that the string which is going over the pulley shall become unequally extended in the horizontal and in the vertical directions until the pulley moves. The excess of the latter force against the first one shall be temporarily compensated by the forces of friction at the axis of the pulley until this excess attains the "limit of plasticity" as in the experiments of *Verchorskij*. Then starts the motion of the pulley and of the weight which lasts until the increase of the extension of the string and the corresponding increase of the deformation of the solid shall not equalise the force of inertia of the falling weight and of the moving pulley. From this moment the force acting on the solid shall temporarily exceed the weight of the load but their difference shall gradually decrease and then change its sign and increase as stated above.

All these circumstances play no or a much smaller role for the regime  $f=0$  as may be clearly seen from the great smoothness of the curve giving  $\chi'$  as function of  $t$  after the load is taken off, in comparison with the curve corresponding to the quasi-permanent force. This lack of constancy is somewhat diminished by gentle taps on the sample before each observation.

The same unsteadiness of the acting force evokes the impossibility of strictly realising the regime  $\chi'=\text{const.}$

<sup>1</sup> It would be interesting to combine the methodology of *Verchorskij* and the methodology of *W. B. Hardy* and *J. P. Hardy* (Phil. Mag 38, 32-55, 1919) who observed the changes of the force of friction between two really dry polished solid surfaces after introduction between those of monomolecular and polymolecular layers of definite liquids.

although in a smaller degree than for the regime  $f = \text{const.}$  because the moving mechanism has several toothed wheels with a great number of teeth.

Still greater difficulties (41, 30—31) are present when we intend to realise the regime  $\chi = \text{const.}$  in order to study the phenomenon of relaxation if we do not recur to optical methods of measuring the existing stress. If we wish to measure these stresses mechanically—*e. g.*, by means of the external forces which could equilibrate these relaxed stresses—we must temporarily change the deformation in order to find by successive trials the equilibrium. Much simpler is the methodology used in some of our experiments on the relaxation at the torsion of lead tubes. We determined the strain which was corresponding this day (the observations were usually made once a day) to the chosen permanent angle of torsion of the tube and then knowing from preceding observations what increase of the angle of torsion could be expected under the action of this stress during a day we diminished the strain on the half of the corresponding expected change of it so that the angle of torsion was a little less than needed for  $\chi = \text{const.}$  during the first half of the following day and a little greater during the second half.

I cannot conclude this article without indicating the great influence of the temperature on the slow deformations of solids. For the typical plastic materials—having a limit of elasticity practically equal to zero and at the same time a rather high value of the co-efficient of viscosity—the change with the temperature of the celerity of deformation under the action of a constant stress may be in the first approximation represented (4, 21) by the following empirical formula

$$v_{t+\theta} = v_t a^\theta \quad \dots \quad \dots \quad (27)$$

whence

$$\eta_{t+\theta} = \eta_t a^{-\theta} \quad \dots \quad \dots \quad (28).$$



For more broad limits of the temperature, the formula (28) must be replaced by more complicated ones,—for instance (21) by

$$\eta_{t+\theta} = \eta_t \cdot 10^{-a\theta + b\theta^2} \quad (29)$$

where  $b$  is small in comparison with  $a$  or in other words the value of  $a$  in the formula (28) is not constant but increases with the lowering of the temperature  $t$ . For ice (3, 5, 8) I have used also the formula

$$\eta_{- \theta} = \eta_0 \left( a + \frac{b}{\theta} \right)^{\theta} \quad \dots \quad (30)$$

The value of  $a$  in the formula (28) is very high for the typical plastic materials, namely, from 1.1 to 1.4 (4) what corresponds to a change of  $\eta$  of 10—40% of its value *at each degree*. For instance I found for pitch at 20° (21, 229)  $a=1.38$  and at 40°  $a=1.23$  and for asphalt at 20°  $a=1.44$  and at 40°  $a=1.30$ .

I may mention also the phenomenon of the “thermal hysteresis of the angular velocity of shear” (21, 203): the velocities at decreasing temperatures are—for asphalt—somewhat smaller than at the same temperatures, but increasing if however the variations of the temperature are not too slow. This is an example—

$$t = 18.51 \ 18.56 \ 18.88 \ 19.15 \ 19.70 \ 18.58 \ 19.04 \ 19.70;$$

$$\tau = 0.085 \ 0.090 \ 0.101 \ 0.109 \ 0.137 \ 0.083 \ 0.095 \ 0.137.$$

For the usual metals the phenomena of internal friction in the strict sense of the word are not yet studied: the stationary regime being perhaps attained only after several years and the so-called “internal friction” studied in the phenomenon of the damping of the torsional vibrations having probably nothing in common with the property which governs

the stationary regimes. From the observations on months-long torsion of a lead tube I found (4) that the difference  $\alpha-1$  is of the order 0.05. I may mention that *Kuznecov* (11) has obtained for rock-salt  $\alpha-1=0.27$ —but for the initial stages of the action of a permanent stress the regime of which differs considerably from the final stationary regime<sup>1</sup>

All these circumstances indicate the necessity to maintain possibly constant the temperature of the rooms where the apparatus for studying the slow transformations of solids have to be placed because these apparatus must have usually dimensions too big for a thermostat. If we take into account that the duration of such experiments is measured by months if not by year, that the variation of the temperature of a *tenth* of a degree can exert a variation of  $3-\frac{1}{2}\%$  of the force or of the deformation, that there exists the “thermal hysteresis,” that this region of physics is almost unexplored, we must at the present time—*faute de mieux*—not reject even the experiments far from the ideal—in so much as this ideal is gradually depicting itself in the very course of such experiments.

<sup>1</sup> V. D. *Kuznecov*, “On the internal friction of lead by great velocities of shear”—R. Phys. Soc, 56, 296-311, 1925 (russ with engl, resume)

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B. T. In. = Bulletin of the Tomsk Technological Institute (Izvestija Tomskago Technologičeskago Instituta).

Comm = Communications on the Scientific-Technical researches in the Republic (Soobščeniya o naučno-techničeskikh rabotach v Respublike).

J. Ap. Ph. = Journal of Applied Physics (Jurnal prikladnoj fiziki).

J. R. Ch. S. = Journal of the Russian Chemical Society (Jurnal russkago chimičeskago obščestva)

J. R. Ph. S. = Journal of the Russian Physical Society (Jurnal russkago fizičeskago obščestva).

M. Od. Un. = Memoirs of the Odessa University (Zapiski Novorossijskago Universiteta).

M. S. = Messenger of Science (vestnik znaniya).

T. R. As. = Transactions of the III Meetings of the Russian Association of Physicists (Trudy III S'ezda Rossijskoj Associacii fizikov).

T. S. N. = Transactions of the Society of Naturalists and Physicians at the Tomsk University (Trudy obščestva estestvoispytatelej i vračej pri Tomskom Universitete).

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## A Discussion of the Available Data on Light-scattering in Fluids.

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### I. DIFFERENT THEORIES OF SCATTERING

In a recent paper on light scattering, M. Y. Rocard<sup>1</sup> has made a comparison of the theories of Ramanathan, King and Gans. For a medium consisting of anisotropic molecules oriented at random, Ramanathan<sup>2</sup> gets for the ratio of the weak component to the strong in the transversely scattered light, when the incident light is unpolarised, the expression

$$r = \frac{6\delta}{\frac{5RT\beta_n}{N} \left( \frac{\nu^2 + 2}{3} \right)^2 + 7\delta} \quad \dots (1)$$

where

$$\delta = \frac{A^2 + B^2 + C^2 - AB - BC - CA}{(A + B + C)^2}$$

A, B, C being the optical moments induced in a molecule when placed in a field of unit intensity parallel respectively to its three principal anisotropic axes ;

R and N are the gas constant and Avogadro number respectively per gram molecule,

<sup>1</sup> *Comptes Rendus*, Aug 3rd, 1925

<sup>2</sup> *Proc Ind Assn. Cultn. Sc.*, viii, pp. 1-22 & 181-198 (1923).



$T$  is the absolute temperature,

$\beta$  in the isothermal compressibility,

$n$  is the number of molecules per unit volume, and

$\nu$  is the refractive index of the medium.

For the total fraction of the incident unpolarised light, scattered transversely per unit volume, per unit solid angle, he gets

$$I = \frac{\pi^2 RT \beta}{18 N \lambda^4} (\nu^2 - 1)^2 (\nu^2 + 2)^2 \cdot \frac{6(1+r)}{6-7r} \quad \dots (2)$$

For isotropic molecules it obviously reduces to the Einstein-Smoluchowski expression.

King's theory,<sup>1</sup> which is also molecular, leads on the other hand to the values<sup>2</sup>

$$r = \frac{6\delta}{5 \frac{RT \beta n}{N} + 7\delta} \quad (3)$$

and

$$I = \frac{\pi^2 RT \beta}{2 N \lambda^4} (\nu^2 - 1)^2 \frac{6(1+r)}{6-7r} \quad (4)$$

Gans,<sup>3</sup> on the other hand, from purely thermodynamical considerations, has obtained an expression for  $r$  in terms of the Kerr constant (Electric double refraction) of the medium :

$$r = \frac{48\pi\nu\lambda B}{\frac{1}{3}\beta(\nu^2 - 1)(\nu^2 + 2)(k - 1)(k + 2) + 56\pi\nu\lambda B} \quad (5)$$

<sup>1</sup> Nature, cxi, p 667 (1923).

<sup>2</sup> King really uses the adiabatic compressibility. However, for the purpose of our present discussion, we shall use the isothermal.

<sup>3</sup> Zests. f. Physik, xvii, p. 353 (1923).

where  $k$  is the dielectric constant and  $B$  is the Kerr constant, as usually defined

$$\left( \epsilon_{\parallel} - \epsilon_{\perp} = \frac{\nu^2 - \nu_1^2}{\lambda E^2} \right).$$

According to Langevin's theory of the Kerr effect, for non-polar molecules, which is the case contemplated by Gans's theory,

$$B = \frac{(\nu^2 - 1)(\nu^2 + 2)}{4\nu\lambda} \left( \frac{k+2}{3} \right)^2 \frac{\Theta}{\frac{A+B+C}{3}} \quad \dots \quad (6)$$

where

$$\Theta = \frac{1}{45} \frac{N}{RT} \left\{ (A-B)(A'-B') + (B-C)(B'-C') + (C-A)(C'-A') \right\}$$

$A'$ ,  $B'$ ,  $C'$  are the constants of electrical anisotropy corresponding to the optical constants  $A$ ,  $B$ ,  $C$ .

The above expression for the Kerr constant, assumes that the principal axes of electrical and optical anisotropy coincide. Now let us make some simplifying assumptions, analogous to those made by Gans in his discussion, regarding the relation between the constants of electrical and optical anisotropy. Thus, let us suppose that

$$\frac{A'}{A} = \frac{B'}{B} = \frac{C'}{C}$$

Then the above ratio

$$\begin{aligned} &= \frac{A' + B' + C'}{A + B + C} \\ &= \frac{k-1}{\nu^2-1} \cdot \frac{k+2}{\nu^2+2} \end{aligned}$$

<sup>1</sup> Langevin's actual expression for  $B$  [*Le Radium*, vii, p. 249 (1910)] refers to the simple case when the anisotropic molecule has an axis of symmetry. The expression given here is a generalisation of Langevin's, taken from Debye, Marx's "*Handbuch der Radiologie*," Bd VI, p. 768

and the expression for the Kerr constant reduces to

$$B = \frac{(k-1)(k+2)(\nu^2-1)(\nu^2+2)N}{120\pi RTn\lambda\nu} \delta \quad \dots (7)$$

Substituting this value in (5) we have

$$\rho_{\text{Gans}} = \frac{6\delta}{\frac{5RT\beta n}{N} + 7\delta}, \quad \dots (8)$$

which is identical with (3).

For I, Gans's theory leads to the same expression as Ramanathan's (Expn 2).

Thus we find that for  $\nu$ , King and Gans get identical values which are, however, different from Ramanathan's, while for I, Ramanathan's expression is the same as Gans's, but different from that of King. It is needless to point out that, in the case of vapours and gases sufficiently rare that  $\nu^2$  is very nearly equal to unity, the different expressions agree.

Recently, measurements have been made in this laboratory, on the scattering constants of a number of vapours and liquids; and it is proposed in the present paper to ascertain how far the different theories fit in with the experimental facts—leaving alone, for the present, all considerations regarding the theoretical merits of the different hypotheses underlying the above theories.

## II. INTENSITY OF THE SCATTERED LIGHT

Table I gives the values of I for a number of liquids, *relative to ethyl ether*, calculated by the two formulæ [(2) and (4)], along with the observed values for comparison.

TABLE I

Liquid	r	Autho- rity	r adopted	I CALCULATED ETHER=1		I OB- SERVED Ether =1	Autho- rity	
				Ramana- than- Gans	King			
Pentane	{ 072 078	{ M L K	{ 075	1 11	1 11	1 14	K	
Isopentane	056	K		1 06	1 06	1 06	K	
Hexane	{ 100 099	{ M. L. K	{ 100	0 99	0 96	{ 1 13 1 00	{ M. L. K	
Heptane	{ 127 100	{ M L(2) K	{ 114	0 95	0 90	1 00	K	
Octane	129	K		0 94	0 89	0 96	K	
$\beta$ -isomyrene	258	K		1 78	1 71	1 54	K	
Ethyl bromide	250	K		1 71	1 55	1 58	K	
Ethylene chloride	36	K		1 60	1 40	1 44	K	
Chloroform <sup>1</sup>	{ 238 242	{ G K	{ 240	1 49	1 31	{ 1 26	K	
	150	R R	{ 150	1 21	1 06			
	150	M(2)						
Carbon tetrachloride ...	{ 045 061	{ G K	{ 053	1 12	0 96	1 02	K	
Carbon bisulphide	{ 64 685	{ G K		16 4	10 9	{ 12 8 13 0	{ M.L. K	
				21 3	14 1			
Acetic acid ...	{ 439 47	{ G K	{ 455	1 43	1 39	1 19	K	
Benzene						2 82	M L	
	47	K		3 90	3 13	3 64	R R	
						3 2	R	
						3 15	K	

<sup>1</sup> It is surprising that the two sets of values for  $r$  for chloroform agreeing perfectly among themselves, should however differ so widely from each other

Liquid	r	Autho- rity	r adopted	I CALCULATED ETHER=1		I OB- SERVED. Ether =1	Autho- rity		
				Ramana- than- Gans	King				
Toluene	{ 490 507 525	M. L G K	51	4 06	3 29	{ 3 21 3 45 3 53	M L R R K		
Ethyl benzene	53	K				4 17	3 37	3 18	K
Meta Xylene	57	K				4 82	3 90	3 87	K
Para Xylene	583	G		5 22	4 23	4 61	K		
Chlorobenzene	58	K	635	5 27	4 09	{ 4 11 4 10	M L K		
Bromobenzene	{ 618 65	G K		7 59	5 59	4 92	K		
Nitrobenzene	74	K		10 0	7 6	10 5	K		
Aniline	60	K		5 10	3 59	3 42	K		
O nitro-toluene	82	K		20	22	9 40	K		
Methyl alcohol	060	K		0 49	0 51	{ 0 54 0 58	M L. R R		
Ethyl alcohol	053	K		0 59	0 58	{ 0 56 0 72 0 58	M.L. R R K		
n-Propyl alcohol	071	K		0 63	0 60	{ 0 73 0 62	M L K		
Isopropyl alcohol	050	K		0 62	0 59	0 60	K		
n-Butyl alcohol	093	K		0 68	0 64	0 65	K		
Isobutyl alcohol	073	K		0 69	0 65	{ 0 79 0 74	M L K		
Trimethyl carbinol	041	K		0 69	0 66	0 60	K		
Amylic alcohol (inactive)	098	K		C 82	0 76	{ 0 84 0 74	M L K		

TABLE I (contd.)

Liquids	$r$	Autho- rity	$r$ adopted	I CALCULATED ETHER = 1		I OB- SERVED, Ether = 1	Autho- rity
				Ramana than- Gans	King		
Allyl alcohol	290	K		1.29	1.18	1.22	K
Benzyl alcohol	62	K		5.20	3.95	2.93	K
Propyl formate	210	K		0.94	0.91	0.94	K
Ethyl acetate	228	M(1)	230	0.97	0.95	0.98	K
	233	K					
	170	G					
Dimethyl ketone	236	K	20	0.85	0.84	0.81	K
Diethyl ketone	18	K		0.88	0.81	1.06	K
Water	0.85	K		0.19	0.19	0.19	M L
						0.19	R R
						0.21	K

*Authorities —*

M (1)—Martin, Journ. Phys. Chemistry, xxiv, p. 478 (1920).

M L—Martin and Lehrman, *ibid*, xxvi, p. 75 (1922).

R R—Raman and Rao, Phil. Mag., xlv, p. 625 (1923).

R—Ramanathan, Phys. Rev., xxi, p. 564 (1923).

M L (2)—Martin and Lehrman, Journ. Phys. Chemistry, xxvii, p. 558 (1923)

M (2)—Martin, *ibid*, xxviii, p. 1284 (1924)

G—R. Gans, *Zeits. f. Phys.* xxx, p. 231 (1924).

K—K. S. Krishnan, Phil. Mag. l, p. 697 (1925).

From the Table we can easily see that in the case of liquids with refractive indices of the same order of magnitude as in ether, the agreement of the values calculated by either formula with the observed values is quite satisfactory; and, as we should expect, there is not much to choose between the two. But in the case of highly refractive liquids (which have also, in general, a large value for  $r$ ), while King's formula continues to be valid, the other formula gives values for  $I$  consistently higher than the observed values.

Of course for a fair comparison of the two expressions for  $I$ , one should take into consideration the absolute values. But here, owing to the extreme smallness of  $I$  (of the order of  $10^{-8}$ ) the uncertainties in the measurements are naturally much greater and the results obtained by different investigators support either theory indifferently. Thus Martin and Lehman,<sup>1</sup> using some intermediary standards, have compared the intensity of the light scattered by liquid ether with that of the incident light and they get for the mercury line 4358 Å<sup>2</sup>

$$I = 9.2 \times 10^{-6}$$

agreeing perfectly with the value  $8.85 \times 10^{-6}$ , given by King's formula, as against  $14.6 \times 10^{-4}$ , given the formula of Ramanathan and Gans.

On the other hand, Raman and Rao,<sup>3</sup> in determining the Avogadro constant from the absolute scattering by distilled water, get values for  $I$  which seem to support Ramanathan-Gans formula. Further, we have the measurements of Raman<sup>3</sup> on the intensity of water in terms of ether vapour, of Ramanathan<sup>4</sup> on saturated ether vapour at different temperatures and also of ether above the critical temperature, in terms of liquid ether, and those of Raman and Ramanathan<sup>5</sup> on carbon dioxide, both liquid and vapour at high pressures, in terms of carbon dioxide at N. T. P., which fit in with Ramanathan-Gans formula.<sup>6</sup>

In view of the above conflicting results, it would be extremely interesting to redetermine the absolute intensity for some liquid, say ether. In spite of the experimental difficulties it ought to be possible at least to decide between the

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Proc. Roy. Soc. A, ci, p. 64 (1922)

<sup>4</sup> *Ibid.*, cii, p. 151 (1922)

<sup>5</sup> Proc. Roy. Soc. A, civ, p. 357 (1923)

<sup>6</sup> We have no reason to doubt the validity of the theoretical expressions for vapours, especially after the recent measurements on atmospheric transparency, the experiments of Lord Rayleigh on the transparency of gases [Proc. Roy. Soc. A, xciv, p. 155 (1918)] and the work of Cabannes (*Journ. de Physique*, Series VI, Tome I, p. 129 (1920) and Daure (*Comptes Rendus*, June 29th, 1925) on the determination of the Avogadro number from gaseous scattering. Hence all the intensity measurements relative to vapours, referred to in the paper, may be considered absolute.

two expressions, since one gives a value for ether about 1.6 times that given by the other. The author proposes to take up the work shortly.

### III. DEPOLARISATION OF THE SCATTERED LIGHT

In Table II are given the values of  $\delta$  (which may be taken as an expression for the anisotropy of the medium), calculated from  $r$  by (1) and (3), as also the values of  $\delta$  calculated from the Kerr constant  $B$  by (7). Since most of the available data for  $B$  refer to the D line, all the calculations have been made for that wave-length. We confine ourselves to the case of non-polar molecules.

TABLE II

Liquid	$r$	$\delta \times 10^3$ calculated from			Autho- rity †	$\delta \times 10^3$ calculated from $B$
		Raman- athan	King (Gans)	$B \times 10^7$ * for D line at 20°C		
Pentane	075	5.0	3.1	050	L	3.1
Isopentane	056	3.7	2.3	050	Ka	3.1
Hexane	100	4.5	2.7	{ 045	S	2.7
				{ 056	L	3.4
Heptane	111	4.0	2.3	{ 071	S	2.7
				{ 105	L	4.0
Octane	129	3.8	2.2	{ 077	S	2.6
				{ 136	L	4.5

\* Where the values given by the investigators are relative to  $CS_2$ , they have been converted to absolute values, using Chaumont's value for  $CS_2 - B = 3.226 \times 10^{-7}$  for the D line and 20°C

† Authorities —

S—Schmidt, *Ann. der Phys.*, vii, p. 112 (1902).

L—Leiser—quoted by Bergholm, *Ann. der Phys.*, lv, p. 511 (1917)

Mc—McComb, *Phys. Rev.*, xxix, p. 525 (1909).

C—Chaumont, *Ann. de Physique*, IX series, iv, p. 61 (1915)

B—Becker, *Ann. der Phys.*, lxxvi, p. 849 (1925).

Ka—Taken from "Beziehungen Zwischen physikalischen Eigenschaften und chemischer Konstitution" by H. Kauffmann, Stuttgart .. 1920, p. 387.



TABLE II (contd.)

Liquid	$r$	$\delta \times 10^3$ calculated from $r$		$B \times 10$ for D line at 20°C	Autho- rity	$\delta \times 10^3$ calculated from B.
		Rama- nathan	King-Gans			
Carbon tetrachloride	053	2.4	1.2	074	Ka	2.6
Carbon bisulphide	085	255	106	3.226	C	84
	04	189	79			
Benzene	47	45	22	593	Mc	18.5
Meta-xylene	57	48	24	858	B	17.5
Para-xylene	583	52	26	74	S	19
				73	L	

When we remember the large variations in the Kerr constant data obtained by different investigators, and the sensitiveness of  $\delta$  to small variations in  $r$  and B, the agreement, in general, between the Kerr constant values of  $\delta$  and the scattering values of  $\delta$ , should be considered satisfactory. Here again, in the case of highly refractive liquids, King-Gans expression seems to give better agreement than Ramanathan's.

#### IV. ANISOTROPY CALCULATED FROM LIQUID AND VAPOUR STATES.

The agreement between the values of the anisotropy calculated from  $r$  and from B for liquids, raises the question how far these values represent the real anisotropy of the individual molecules, as contemplated by the molecular theories. Of course in the vapour state, where the molecules are sufficiently far apart to exert any mutual influence, we may reasonably suppose that the theoretical formula gives the real anisotropy of the molecules. The values of  $\delta$  calculated from the liquid and vapour states are given in Table III for comparison.

TABLE III

Substance	liquid	$\delta \times 10^3$ calculated from liquid		vapour	Authority	vapour adopted	$\delta \times 10^3$ calculated from vapour
		Ramanathan	King-Gians				
Pentane	075	5.0	3.1	{ 012	R	{ 012	10.1
				{ 012	C. G.		
				{ 028	R. R.	{ 027	23
				{ 025	V		
Isopentane	056	3.7	2.3	012	C. G.		10.1
Hexane	100	4.5	2.7	{ 015	C. G.		12.7
				{ 021	Rn		18
Heptane	114	4.0	2.3	031	Gn		27
Octane	129	3.8	2.2	027	Gn		23
$\beta$ -isomylene	258	20	12.1	061	Gn		55
Ethyl bromide	250	22	12.4	032	Rn		28
Chloroform	{ 240	15.7	8.4	{ 030	R	031	27
	{ 150	8.6	4.6		Gn		
Carbon tetrachloride	053	2.4	1.2	019	Gn		16
Carbon bisulphide	685	255	106	{ 120	R	143	143
	64	189	79	{ 167	Gn		
				{ 143	Rn		
Ethyl ether	080	5.3	3.2	{ 032	Gn	031	27
				{ 030	Rn		
				{ 068	R. R.		
Benzene	47	45	22	{ 066	Gn	067	61
				{ 067	Rn		
Toluene	51	43	22	064	Gn		58
m-Xylene	57	48	21	067	Gn		61
Chlorobenzene	58	55	27	078	Gn		72

TABLE III (*contd*)

Substance	liquid	$\delta \times 10^3$ calculated from liquid		vapour	Autho- rity	vapour adopted	$\delta \times 10^3$ calculated from vapour
		Rama- nathan	King- Gans				
Bromobenzene	635	69	31	078	Gn		72
Nitrobenzene	74	115	53	056	Rn		50
Aniline	60	46	20	049	Rn		43
Methyl alcohol	060	6.2	3.9	027	Gn		23
Ethyl alcohol	053	3.6	2.2	017	Gn		14.5
n Propyl alcohol	071	3.5	2.1	020	Gn		17
Iso-propyl alcohol	050	2.5	1.5	019	Gn		16
n Butyl alcohol	093	3.6	2.1	020	Gn		17
Isobutyl alcohol	073	3.0	1.7	019	Gn		16
Allyl alcohol	296	23	12.7	052	Gn		46
Propyl formate	210	9.7	5.7	035	Gn		30
Ethyl acetate	230	12.4	7.4	034	Gn		29.5
Dimethyl Ketone	200	14.1	8.6	048	Gn		42

*Authorities --*

R—Lord Rayleigh, Proc. Roy. Soc., A, xcv, p. 155 (1918)

V—R. Venkateswaran, Trans. Chem. Soc., cxxi, p. 2655 (1922).

R. R.—Raman and Rao, Phil. Mag., xlv, p. 426 (1923).

Gn—A. S. Ganesan, Phil. Mag., xlix, p. 1216 (1925).

C.G.—Cabannes and Gauzit, *Journ. de Physique et le Radium*, Series VI, Tome vi, p. 182 (1925).

Rn—K. R. Ramanathan—unpublished.

One can easily see that, even though in the case of high depolarisation liquids like benzene, its derivatives, carbon bisulphide, etc., the anisotropies calculated from the liquid and vapour states are more or less the same, in other cases the "effective anisotropy" in the liquid state is much smaller

than the anisotropy in the vapour state. Probably it is due to *temporary* molecular groupings, of the kind suggested by Raman,<sup>1</sup> having a higher degree of optical symmetry than the individual molecules. This change in "effective anisotropy" in the liquid state can be explained in a general way. Taking for example a long molecule like pentane, when there is a close packing of the molecules, as in the liquid state, the influence on any atom in the molecule, of the atoms in the neighbouring molecules might compare favourably with the influence of the atoms in the same molecule; and this might conduce to a greater optical symmetry of the molecule. But in the case of a molecule like benzene, where the influence of the atoms in the same molecule is already large, the contributions from the atoms of the neighbouring molecules might be small in comparison, in which case, the influence of close packing on the anisotropy would also be small.

It would have been interesting to confirm from Kerr constant data this change in the "effective anisotropy" as we pass from the vapour to the liquid. But we have not sufficient data for  $B$  for vapours. However, we have seen how  $\delta$  from <sup>A</sup> liquid agrees satisfactorily with  $\delta$  from <sup>B</sup> liquid, and there is no reason why  $\delta$  from <sup>A</sup> vapour should not agree with  $\delta$  from <sup>B</sup> vapour.<sup>2</sup>

<sup>1</sup> Nature cxi, p 428 (1923)

<sup>2</sup> For  $\text{CO}_2$ ,  $\nu = 107$  [mean of the values 117 of Rayleigh, 106 of Raman and Rao and 098 of Cabannes and Granier] gives

$$\delta = 102,$$

while Szivessy's value [*Zeits. f Physik*, xvi, p. 323 (1924)] for the Kerr const.,  $B = 24 \times 10^{-10}$  per atm., for the D line and  $17.5^\circ\text{C}$  (which agrees closely with Hansen's  $23 \times 10^{-10}$ ) gives

$$\delta = 077$$

In the case of  $\text{N}_2\text{O}$ , the value  $\nu = 143$  of Raman and Rao gives  $\delta = 143$ , and the value of Cabannes and Granier  $\nu = 122$  gives  $\delta = 118$ . From Hansen's value for the Kerr const.,  $B = 48 \times 10^{-10}$  per atm. (Szivessy's report in *Jahrbuch der Radioaktivitat*, 1919)  $\delta$  comes out to be 125.

The other vapours for which we have data both for  $B$  and for  $\nu$ , have polar molecules and they will be discussed in a later paper.

## V. VARIATION OF THE ANISOTROPY IN LIQUIDS WITH TEMPERATURE

We have seen how the anisotropy calculated from the liquid state is in general, much smaller than that calculated from the vapour. Now in the case of some liquids, *viz.*, ether,<sup>1</sup> pentane,<sup>2</sup> heptane,<sup>3</sup> benzene,<sup>3</sup> and carbon bisulphide<sup>4</sup> the depolarisation of the scattered light has been studied for different temperatures up to the critical point; and with the help of these data, we can follow continually the change in the anisotropy as we pass gradually from the liquid to the gaseous state. But there is one difficulty in calculating  $\delta$  at higher temperatures; we have no compressibility measurements for some of these liquids. For ether and pentane,  $\beta$  can be calculated from the pressure-volume curves of Ramsay and Young<sup>5</sup> and Rose—Innes and Young<sup>6</sup> respectively, and these values have been used in the calculations below. But for the other three liquids we have no such data. Also the equations of state cease to give even rough approximations for  $\beta$  as we approach the critical point. However, we have seen in Part II that the values of the intensity of the scattered light calculated by King's formula [Eqn. (4)] agree satisfactorily with the observed values. *Assuming the validity of that expression*,  $\beta$  has been calculated for heptane and benzene (relative to the known compressibilities at room temperature)

<sup>1</sup> K R Ramanathan, Proc. Roy Soc, A, cii, p. 151 (1922).

<sup>2</sup> R Venkateswaran, Trans Chem. Soc, cxxi, p. 2655 (1922)

<sup>3</sup> Martin and Lehrman, Jour Phy Chem, xxvii, p. 558 (1923)

<sup>4</sup> K R Ramanathan, not published

<sup>5</sup> Phil Trans. Roy Soc, A, clxxviii, p. 57 (1887)

<sup>6</sup> Phil Mag, V series, xlvii, p. 355 (1899)

from the corresponding observed values of the intensity of the scattered light.

When we come to  $\text{CS}_2$ , Amagat's values<sup>1</sup> for the compressibility extend only up to  $100^\circ \text{C}$ ; and for higher temperatures, we have no data even for the intensity of the scattered light from which to calculate  $\beta$  as in the case of heptane and benzene. Thus, for want of other means of calculating the compressibility, it was assumed that the compressibility of  $\text{CS}_2$  at any required temperature is the same as the compressibility of liquid  $\text{CO}_2$  at the same "reduced temperature" ( $T/T_c$ ). For the latter substance, we have of course the pressure—volume measurements of Jenkin<sup>2</sup> at different temperatures.

The other data were taken from Landolt-Börnstein Tables (1923). The refractive indices at higher temperatures were calculated from the experimental values of the molecular refractivity at the room temperature and the known densities, using the Lorentz-Mossotti relation.

For  $\text{CS}_2$ , no direct measurements of the density are available for higher temperatures, and the values were therefore interpolated between the known densities at ordinary temperatures and at the critical point, using for the purpose the temperature (reduced) variation curve of the density of liquid  $\text{CO}_2$ .

The calculated values of  $\delta$  are given in Tables IV to VIII. In the case of ether, pentane and  $\text{CS}_2$ , the authors' values were plotted and smoothened.

<sup>1</sup> Taken from "*Piezochemie*," by Cohen and Schut, Leipzig, 1919, pp 112 and 100.

<sup>2</sup> Proc. Roy. Soc. A., xcviii, p 170 (1920)

TABLE IV—*Ether*.

Temp °C	<i>r</i>	$\delta \times 10^3$ Calculated	
		Ramanathan	King-Gans.
35	080	5.8	3.6
60	079	7.2	4.5
90	074	9.2	6.0
100	071 <sub>6</sub>	10.5	6.9
150	024	16.0	11.3
175	015	19.7	14.6
185	014	40	31
190	013	115	90
Critical temp = 193.6°C		$\delta \times 10^3$ from vapour = 27	

TABLE V—*n-Pentane*.

Temp °C	<i>r</i>	$\delta \times 10^3$ Calculated	
		Ramanathan	King-Gans
30	072	5.2	3.2
120	048	12.0	8.1
140	023	7.1	4.9
150	017 <sub>6</sub>	7.0	4.9
160	015	7.8	5.6
170	014	11.4	8.3
Critical temp = 197.2°C		$\delta \times 10^3$ from vapour = 10.1	

TABLE VI—*n*-Heptane.

Temp °C	$r$	$\delta \times 10^3$ Calculated	
		Ramanathan	King Gans
20	127	4.6	2.7
100	100	4.0	2.5
200	088	4.8	3.3
225	026	5.9	4.2
240	020	7.2	5.3
250	017	8.6	6.4
260	0165	11.6	9.0
Critical temp = 266.85°C		$\delta \times 10^3$ from " vapour = 27	

TABLE VII—Benzene.

Temp °C	$r$	$\delta \times 10^3$ Calculated	
		Ramanathan	King-Gans
20	485	49	24
100	394	50	26
200	154	40	24
250	081	46	30
260	045	63	42
270	025	68	47
280	015	142	102
Critical temp = 288°C		$\delta \times 10^3$ from " vapour = 61	



TABLE VIII—*Carbon bisulphide.*

Temp °C	$r$	$\delta \times 10^3$ Calculated	
		Ramanathan	King-Gans
30	67	248	101
100	545	147	66
150	42	100	49
180	325	137	71
200	26	153	82
210	225	131	72
Critical temp = 273°C		$\delta \times 10^3$ from vapour = 143.	

It is necessary here to draw attention to the serious experimental difficulties in the measurement of the depolarisation of the light scattered by liquids under very high pressures. The unavoidable strain produced in the glass walls or windows, as the case may be, through which observations are made, will introduce errors, which will be most conspicuous near the critical point, where the weak component is very small. When we remember also the difficulties of securing good back-ground in high pressure work, it is needless to point out that, in spite of the precautions taken by the investigators, the values for  $r$  near the critical temperature can only be taken as approximate.

However, without laying any stress on the actual calculated values of  $\delta$ , we can see in a general way that in the case of ether, pentane and heptane, as the temperature is increased, the anisotropy, according to either formula, also increases, continually approximating to the value calculated from the vapour state, but not actually reaching it even near the critical point. For benzene, King-Gans formula leads to

the same conclusion; while for benzene according to Ramanathan's formula and for  $\text{CS}_2$  according to either formula, the calculated values of  $\delta$  at different temperatures are almost of the same order of magnitude as in the vapour, and the variations of individual values are more or less indifferent.

If, as we have supposed in Part IV, the smaller value of the anisotropy calculated from the liquid state, as compared with the value calculated from the vapour state, is due to the influence of the atoms of the neighbouring molecules, consequent upon the closer packing in the liquid state, it is not difficult to understand this continual approximation of  $\delta$  liquid to  $\delta$  vapour as we approach the critical temperature.

## VI. SUMMARY AND CONCLUSION

1. The theories of light-scattering of Ramanathan, King and Gans lead to different expressions for the intensity and the depolarisation of the scattered light. Attempt is made to test how far they fit in with experimental facts.

2. Relative measurements of the intensity, agree much better with King's expression than with Ramanathan-Gans expression. However the evidence of absolute measurements is not unanimous.

3. The anisotropy calculated from scattering measurements agrees satisfactorily with that calculated from Kerr constant, King-Gans formula giving slightly better agreement.

4. The anisotropy calculated from the liquid state is, in general, smaller than the value calculated from the vapour. A general explanation is suggested.

5. The anisotropy calculated from the liquid is found to increase with rise of temperature, continually approximating to the anisotropy in the vapour state, but not actually reaching it even near the critical point

The author's thanks are due to Prof. C. V. Raman for his kind suggestions.

210, BOW BAZAR STREET, }  
CALCUTTA, }  
26th December, 1925. }

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## On the Total Reflexion of Light.

By

PROF. C. V. RAMAN, F.R.S.

### *I. Introduction.*

It has long been known that the explanation of the phenomenon of total reflexion of light on the principles of the wave-theory involves the existence in the second medium of a disturbance which penetrates beyond the boundary to a depth depending on the angle of incidence and diminishing exponentially as the perpendicular distance of the point of observation from the boundary is increased. Stokes<sup>1</sup> showed how the expression for this disturbance which he designated as a *superficial undulation* may be derived directly from the Fresnel formulæ for the intensities of the reflected and refracted beams of light, and applied the same method to the investigation of the appearance of the central spot in Newton's Rings formed beyond the critical angle of incidence. A discussion of the problem on the principles of the electromagnetic theory is given in Drude's<sup>2</sup> Theory of Optics, where the question of the flow of energy in the second medium is also considered on the basis of Poynting's Theorem. That the superficial disturbance in the second medium must be a physical reality is indicated by the consideration that it is

<sup>1</sup> Mathematical and Physical Papers, Vol II, p 57

<sup>2</sup> English Translation, p 200

closely related to the changes of phase occurring in total reflexion and that the same theory which predicts it also gives a quantitative explanation of the elliptic polarisation actually observed when light plane-polarised in any azimuth is totally reflected.<sup>1</sup> Further, the phenomena of Newton's Rings beyond the critical angle, already mentioned, and the fact that small particles placed in contact with the boundary in the second medium are observed to scatter light when viewed through a microscope are usually regarded as confirming the theory. Some doubt has however been thrown on the usual treatment in a recent theoretical paper<sup>2</sup> by Sir Arthur Schuster who appears to hold that the assumption made in the theory of an infinitely extended surface is essentially illegitimate. Moreover, the present writer has recently shown<sup>3</sup> that by using intense monochromatic light (the green or violet line of the mercury arc), and an ordinary spectro-scope, the light emerging from the second face of a prism on which the light was incident at an angle greater than the critical angle could be readily observed. Photographs showing the disturbance emerging into the second medium were published, and they clearly indicated that the effect observed was due to the limitation of the aperture of the pencil incident on the surface and was thus primarily a phenomenon of diffraction. Similar effects were also observed with a Lummer-Gehrcke plate when light was incident within the plate at an angle greater than the critical angle. These effects clearly indicate that diffraction does play a part in the phenomena of total reflexion, and it becomes necessary to consider the matter afresh in the light of the new

<sup>1</sup> So far as the writer is aware, no measurements of the *absolute* change of phase of the light-vector for the two principal components taken *separately* have been made for the case of total reflexion at any angle. For the case of total reflexion at grazing incidence however, Bevan has made observations by the method of Lloyd's interference-fringes (Phil. Mag., Oct. 1907), which are in agreement with theory.

<sup>2</sup> Proc. Roy. Soc. A, 107, p. 15.

<sup>3</sup> Phil. Mag., 6th Series, Vol. 50, p. 812.

experimental evidence now available. It is proposed in this paper to consider, *de novo*, the phenomena of total reflexion from the point of view of diffraction theory.

## 2. *Application of the Fresnel-Huyghens Principle.*

In the general explanation of total reflexion first given on the principles of the wave-theory by Huyghens, the elementary parts of the boundary between the two media are regarded as the source of secondary wavelets emerging into both media. That there is no refracted wave in the second medium though the boundary is fully illuminated is a consequence of the fact that no common envelope can be drawn to the wavelets emerging into it. There is little doubt that the more recondite phenomena accompanying total reflexion may also be explained by following up Huyghens's original line of thought and applying the principle of interference. In particular, the disturbance existing in the second medium at points close to the boundary, and the diffraction effects arising from the finiteness of the illuminated area should both be capable of determination in this way.

The first step in such a treatment is the marking out of the Fresnel zones on the boundary between the two media. When this is of limited area and the point at which the effect is to be determined is far away from it, the Fresnel zones obviously become parallel rectilinear strips on the surface, and the determination of the integrated effect due to all the zones follows the ordinary methods of diffraction theory. We find in fact that the surface on which light is incident beyond the critical angle and is "totally" reflected sends out into the second medium streamers of light giving rise to diffraction patterns in the usual way. These diffraction-patterns differ however from those of the ordinary kind in being strongly asymmetrical in character and also "truncated," that is to say, they consist only of certain

outlying and relatively faint parts of the diffraction-patterns associated with the forms of aperture used, the principal and relatively intense parts being absent. For, none of the Fresnel zones included within the area correspond to a pole or region of stationary phase. Since the light thus streaming into the second medium represents energy, the reflection occurring at the boundary technically ceases to be total, though practically, the departure from totality is negligibly small, unless the aperture is very small or the incidence is only slightly greater than the critical angle. The streamers of light emerging into the second medium, have, as in all cases of diffraction, their origin at the margins of the diffracting area. The front and rear parts of the boundary are, at distant points, equally operative. The observations of Dr. Chuckerbutti<sup>1</sup> and those of the present writer already quoted on the effects observed with a surface bounded by parallel edges entirely agree with these indications of theory. One special feature which comes into prominence in these observations and which deserves to be emphasised is that the intensity of the diffraction-pattern is zero at all distant points lying in the plane of the boundary when produced, that is to say, at all points from which when viewed, the angular aperture of the illuminated area is zero. As we may move away from this plane, the diffraction-pattern steadily gains in intensity. This may be regarded as an effect due to the variation of the "obliquity-factor" of diffraction, and is, in fact, thus explained in the papers already quoted. It has the influence of altering enormously the relative intensities of the diffraction-bands and making them very different from those calculated in the usual way.

### 3. *Disturbance at Points close to the Surface.*

The same method of treatment may be applied to the other case of interest, namely, the effect at a point in the

<sup>1</sup> Proc Roy Soc A., 99, p 503, 1921.

second medium very close to the illuminated area. It is a fact of observation that for angles of incidence exceeding the critical angle, the illumination dies away very quickly as we move away from the surface and the chief interest is thus in determining the effect at points lying within a distance of a few wave-lengths from it. At such small distances, the usual approximate methods of finding the effect due to the Fresnel zone and of integrating the same over the whole of the surface of resolution are not quite rigorous. Nevertheless, as will be shown below, they may be applied with success to the elucidation of the particular case under consideration. In fact, even by merely considering the geometrical form of the Fresnel zones, a considerable insight into the problem may be obtained.

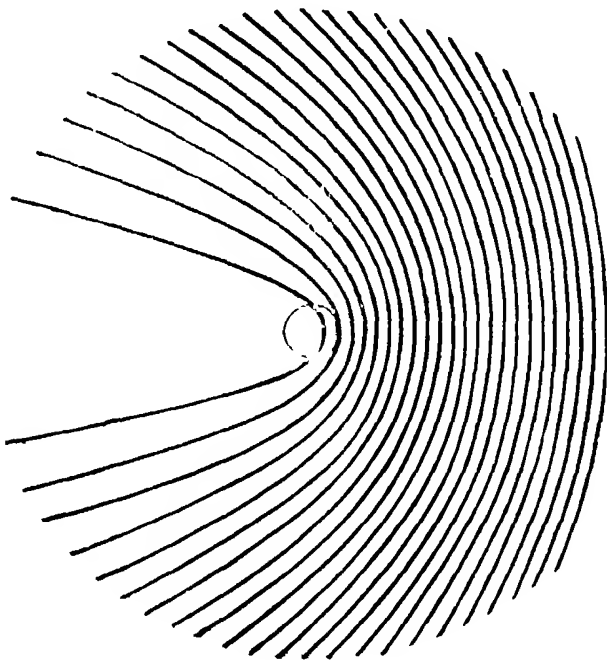


Fig. 1.

Fresnel zones on surface. Incidence =  $45^\circ$  = Critical Angle Point of observation is on the surface,



The form of the Fresnel zones over the surface for any angle of incidence and for any point of observation may be readily mapped out in the following way. From the point of observation, a perpendicular may be dropped on the surface, and round its foot as centre, a set of circles spaced at half-period intervals from the point of observation are drawn. Crossing these are drawn a set of equidistant straight lines perpendicular to the plane of incidence and spaced at such intervals that the distance from one straight line to the next corresponds to a change of phase of the incident waves of half a period. The circles may be numbered, commencing from the centre outwards, 0, 1, 2, 3, 4, 5, etc. The straight line passing through the centre may be numbered 0, and those to the right of it, 1, 2, 3, 4, etc., and those to the left of it  $-1, -2, -3, -4$ , etc. The points of intersections of the circles and straight lines are then marked with the sum of the index-numbers corresponding to the particular circle and straight line cutting at each such point. These index-numbers represent the total difference of path between the secondary waves reaching the point of observation from the nearest element of the surface and from any other. Smooth curves may now be drawn free-hand or with the aid of a flexible steel strip through all the points having identical index-numbers. Very instructive diagrams may be obtained in this way for any specified angle of incidence and for any assigned value of the perpendicular distance from the boundary, and they give accurately the form of the Fresnel zones.

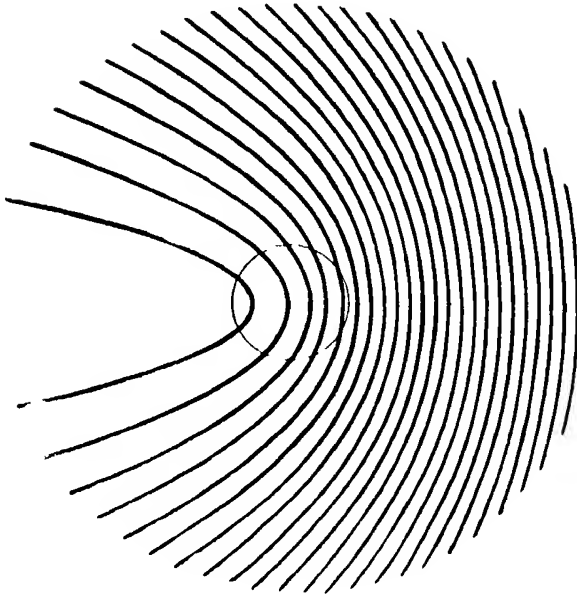


Fig. 2.

Fresnel zones on surface Incidence  $= 45^\circ =$  Critical Angle. Point of observation is  $\lambda$  above the surface.

The geometrical form of the curves drawn in this way shows the following general features. The zones for all angles of incidence in excess of the critical angle are approximately hyperbolic in form. The fact that they are not closed curves indicates that for no point of observation does the surface present any pole or region of stationary phase. The curvature of the lines is most marked for points of observation near the surface; as the distance is increased, the lines become more and more nearly straight. The spacing of the zones draws a striking diminution as we pass in the plane of incidence from negative to positive values of  $x$ , that is, from the left to the right of the foot of the perpendicular drawn from the point of observation. This change in the spacing is the more sudden, the smaller is the distance of the point of observation measured perpendicularly from the boundary. It is largest at the critical angle and diminishes with increasing

angle of incidence. Figs. 1, 2, 3 and 4 represent the form of the Fresnel zones for particular cases and illustrate the foregoing remarks. Figs. 1 and 2 represent the case of incidence at the critical angle  $45^\circ$  and Figs. 3 and 4 for incidence at  $60^\circ$ . The refractive index  $\mu$  is taken as 1.414. In Fig. 1 and Fig. 3 the point of observation is on the surface. In Fig. 2 it is  $\lambda$  above from the surface and in Fig. 4,  $4\lambda$  above the surface. The centre of the smallest unit index circle drawn in each case is the foot of the perpendicular from the point of observation.

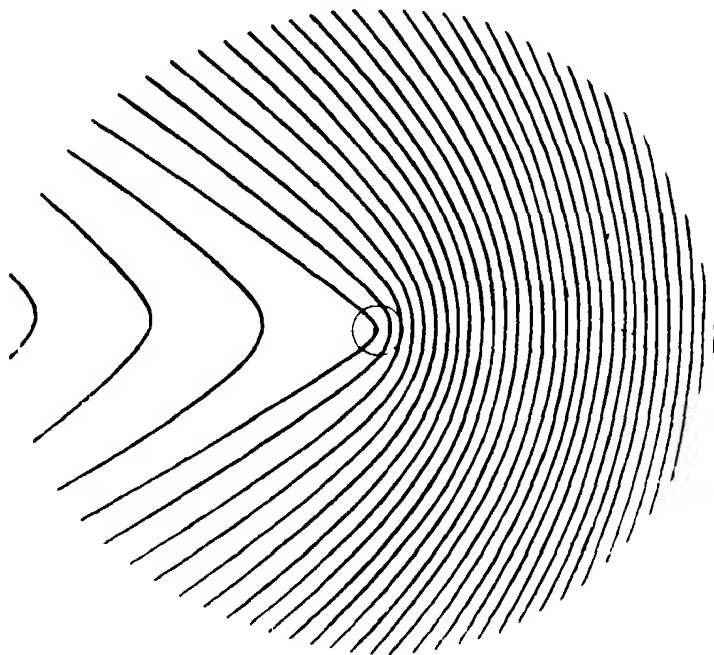


Fig. 3.

Fresnel zones on surface Incidence =  $60^\circ$  Point  
of observation is on the surface.

When we proceed to sum up the effects of the different Fresnel zones, taking into account the varying distances from the point of observation and the varying obliquities, we

should obtain an idea of the way in which the residual effect observed in the second medium varies with the point of observation. Viewed in this way, it is seen that the penetration of the disturbance into the second medium in "total reflexion" may always be regarded as a diffraction-effect. It is important however to determine what part of the effect arises from the outermost parts of the surface and what part from the area closest to the point of observation.

If the Fresnel zones had been uniformly spaced to the right and left of the foot of the perpendicular from the point of observation, they would have annulled each other's effects and given zero as the resultant disturbance. Actually however, as we have seen, there is a change in the spacing as we pass from left to right which is the more sudden, the closer we approach the surface between the two media. The summation over the Fresnel zones would therefore give a resultant effect which is the larger, the more nearly the point of observation approaches the surface. This effect arises from the part of the surface nearest the point of observation, and may be identified with the "superficial undulation" of Stokes and other writers. Since the change in the spacing of the Fresnel zones is most marked when the incidence is just at the critical angle and diminishes rapidly as the incidence is increased, we should expect the resultant effect to diminish in the same way. This is in agreement with the "superficial undulation" formula. We have already seen that the obliquity-factor of diffraction becomes vanishingly small when the angular aperture of the surface as viewed from the point of observation approaches zero. When the point of observation is sufficiently close to the surface, the obliquity becomes practically  $90^\circ$  for all the elements of the surface except those nearest to it. It follows that when the integration is carried out over all the Fresnel zones, the marginal parts of the surface contribute nothing and may be neglected.

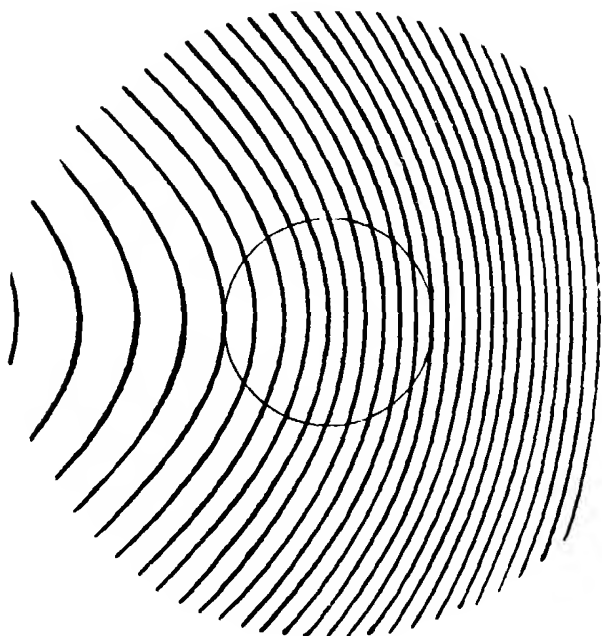


Fig. 4.

Fresnel zones on surface    Incidence at  $60^\circ$ .    Point of observation  
4γ above the surface.

*Analytical Treatment of the Problem.*

The preceding discussion indicates that the superficial undulation in the second medium is a diffraction-effect which arises, not from the margins of the illuminated area, but from the part of the area nearest the point of observation. This may be confirmed by mathematical analysis which indeed shows that the expected effect diminishes exponentially with the distance according to the law already derived from other considerations.

The diffraction integral expressing the effect at any point may easily be written down if we know the law of the secondary wave. The elementary disturbances arising from an area held obliquely to the wave-front have been expressed mathematically in Kirchhoff's well-known formulation of Huyghens's

principle. As has been remarked by various writers, however, Kirchoff's expression is not a unique solution of the problem, as an infinite number of formulæ for the law of the secondary wave may be written down, all of which express correctly the disturbance in free space arising from specified light-sources. In our case, we are, moreover, dealing not with free space, but with the effects observed in the vicinity of a surface of separation between two media. The law of the secondary wave for this case has yet to be determined. For our present purpose, it is sufficient to proceed in the usual simple way and assume that the amplitude of the secondary wave is proportional to the area of the element from which it is sent out and inversely as the product of the wave-length and the distance of the element from the point of observation, and ignore all consideration of the obliquity factor. Let the surface be taken as coinciding with the  $xy$  plane, and the plane of incidence be taken as the  $xz$  plane. Further, let the point of observation be assumed to be on the  $Z$ -axis at a distance  $Z$ , from the origin, the latter being thus on the surface at the foot of the perpendicular drawn from the point of observation. Let  $r$  be the distance of an elementary area on the surface from the origin.

An element of area on the surface is  $rdrd\theta$  and the resultant effect is

$$\text{Const.} \int_0^\infty \int_0^{2\pi} \frac{A}{\lambda(z^2 + r^2)^{\frac{3}{2}}} \cos \frac{2\pi}{\lambda} \{Vt - (z^2 + r^2)^{\frac{1}{2}} - \mu \sin \phi \cos \theta + \epsilon\} r dr d\theta$$

where  $\mu$  is the refractive index of the first medium, the second medium being assumed to be free space,  $\phi$  is the angle of incidence on the surface, and  $\theta$  is the angle which the radius vector  $r$  drawn on the surface makes with the plane of incidence.  $\epsilon$  is the phase difference between the primary disturbance and the secondary waves to which it gives rise.

The integral is assumed to be taken over a sufficiently extended area. It is obvious from physical considerations that the expression must give results which differ entirely in character according as

$$\mu \sin \phi \lesseqgtr 1,$$

that is, according as the incidence is less or greater than the critical angle. This agrees, as we shall see presently, with the actual results of integration.

Integrating with respect to  $\theta$  and writing

$$2\pi/\lambda \cdot (Vt + \epsilon) = \chi,$$

for shortness, the expression reduces to the form

$$\text{Const} \int_0^\infty \frac{2\pi A}{\lambda(r^2 + z^2)^{\frac{1}{2}}} \cos \left\{ \chi - 2\pi/\lambda \cdot (r^2 + z^2)^{\frac{1}{2}} \right\} J_0(2\pi/\lambda \cdot \mu \sin \phi) r dr.$$

When  $z$  is put equal to zero, that is, on the surface itself, the expression reduces to

$$\begin{aligned} \text{Const} \frac{2\pi A}{\lambda} \left[ \cos \chi \int_0^\infty \cos 2\pi r/\lambda \cdot J_0(2\pi r/\lambda \cdot \mu \sin \phi) dr \right. \\ \left. + \sin \chi \int_0^\infty \sin 2\pi r/\lambda \cdot J_0(2\pi r/\lambda \cdot \mu \sin \phi) dr \right] \end{aligned}$$

The integrals appearing within the square brackets are well-known standard forms, the values of which depend on whether  $\mu \sin \phi$  is greater or less than unity. If  $\mu \sin \phi < 1$  the first integral vanishes and the second becomes equal to

$$(1 - \mu^2 \sin^2 \phi)^{-\frac{1}{2}}$$

whereas if  $\mu \sin \phi > 1$ , the second integral vanishes and the first becomes equal to

$$(\mu^2 \sin^2 \phi - 1)^{-\frac{1}{2}}$$

The case  $Z=0$  corresponds to the surface of separation and in order that our result might reduce to the primary disturbance on the surface, the constants expressing the law of secondary wave must be suitably chosen. It is necessary to assume different values for them in the two cases:

$$\text{If } \mu \sin \phi < 1, \text{ Const} = \sqrt{1 - \mu^2 \sin^2 \phi} \\ \text{and } \epsilon = \pi/2$$

$$\text{If } \mu \sin \phi > 1, \text{ Const} = \sqrt{\mu^2 \sin^2 \phi - 1} \\ \text{and } \epsilon = 0$$

We shall now substitute these values in the general expression, considering the two cases separately.

#### Case I.

Incidence less than the critical angle and  $\mu \sin \phi < 1$

The expression for the light-disturbance given above involves the evaluation of two integrals, namely

$$\int_0^\infty \sin 2\pi/\lambda \cdot (r^2 + Z^2)^{\frac{1}{2}} J_0(2\pi/\lambda \cdot r\mu \sin \phi) (r^2 + Z^2)^{-\frac{1}{2}} r dr$$

and

$$\int_0^\infty \cos 2\pi/\lambda \cdot (r^2 + Z^2)^{\frac{1}{2}} J_1(2\pi/\lambda \cdot r\mu \sin \phi) (r^2 + Z^2)^{-\frac{1}{2}} r dr$$

Using the well-known formulæ

$$J_{-\frac{1}{2}}(x) = \sqrt{\frac{2}{\pi x}} \cos x, \text{ and } J_{\frac{1}{2}}(x) = \sqrt{\frac{2}{\pi x}} \sin x$$

the two integrals under consideration are found to be special cases of a very general type of integral involving products of Bessel functions which has been discussed by Sonine.<sup>1</sup> We

<sup>1</sup> Math Annalen, Band XVI, p 1 See also Nielsen, Cylinderfunction, 1904.



shall however adopt a different method of evaluation. Lamb has proved the following formula :

$$\int_{-\infty}^{\infty} e^{\alpha(\xi^2 - \eta^2)^{\frac{1}{2}}} J_0(\beta\xi) (\xi^2 - \eta^2)^{-\frac{1}{2}} \xi d\xi = \frac{e^{-i\eta(\alpha^2 + \beta^2)^{\frac{1}{2}}}}{(\alpha^2 + \beta^2)^{\frac{1}{2}}}$$

In this relation, write  $\xi = r$  and  $\eta^2 = -Z^2$ . Also put

$$\beta = 2\pi/\lambda \mu \sin \phi \text{ and } \alpha^2 = -(2\pi/\lambda)^2.$$

The equation then stands thus:

$$\begin{aligned} & \int_0^{\infty} e^{-2\pi i/\lambda (r^2 + Z^2)^{\frac{1}{2}}} J_0(2\pi/\lambda \mu \sin \phi) (r^2 + Z^2)^{-\frac{1}{2}} r dr \\ &= -i \lambda/2\pi (1 - \mu^2 \sin^2 \phi)^{-\frac{1}{2}} e^{-iZ \cdot 2\pi/\lambda (1 - \mu^2 \sin^2 \phi)^{-\frac{1}{2}}} \end{aligned}$$

Separating the real and imaginary parts we have

$$\begin{aligned} & \int_0^{\infty} \sin 2\pi/\lambda (r^2 + Z^2)^{\frac{1}{2}} J_0(2\pi/\lambda \mu \sin \phi) (r^2 + Z^2)^{-\frac{1}{2}} r dr \\ &= \lambda/2\pi (1 - \mu^2 \sin^2 \phi)^{-\frac{1}{2}} \cos \left\{ 2\pi/\lambda \cdot Z (1 - \mu^2 \sin^2 \phi)^{\frac{1}{2}} \right\} \end{aligned}$$

and

$$\begin{aligned} & \int_0^{\infty} \cos 2\pi/\lambda (r^2 + Z^2)^{\frac{1}{2}} J_0(2\pi/\lambda \mu \sin \phi) (r^2 + Z^2)^{-\frac{1}{2}} r dr \\ &= -\lambda/2\pi (1 - \mu^2 \sin^2 \phi)^{-\frac{1}{2}} \sin \left\{ 2\pi/\lambda \cdot Z (1 - \mu^2 \sin^2 \phi)^{\frac{1}{2}} \right\} \end{aligned}$$

These results are confirmed by comparison with the general formulæ given by Sonine and Nielsen. Substituting

the values of the integrals in the expression for the disturbance in the second medium, we find that the latter reduces to

$$A \cos 2\pi/\lambda (Vt - r\mu \sin \phi - Z\sqrt{1 - \mu^2 \sin^2 \phi})$$

which is of the same form as the ordinary expression for the refracted wave.

*Case II. Incidence at more than the critical angle, and  $\mu \sin \phi > 1$*

With the same substitutions as before, Lamb's formula now reads thus :

$$\begin{aligned} & \int_0^\infty e^{-2\pi i/\lambda (r^2 + Z^2)^{\frac{1}{2}}} J_0(2\pi/\lambda \cdot r \cdot \mu \sin \phi) (r^2 + Z^2)^{-\frac{1}{2}} r dr \\ &= \lambda/2\pi (\mu^2 \sin^2 \phi - 1)^{-\frac{1}{2}} e^{-Z \frac{2\pi}{\lambda} (\mu^2 \sin^2 \phi - 1)^{\frac{1}{2}}} \end{aligned}$$

Separating the real and imaginary parts, we have

$$\int_0^\infty \sin \frac{2\pi}{\lambda} (r^2 + z^2)^{\frac{1}{2}} J_0(z\pi/\lambda \cdot r \cdot \mu \sin \phi) (r^2 + z^2)^{-\frac{1}{2}} r dr = 0$$

and

$$\begin{aligned} & \int_0^\infty \cos \frac{2\pi}{\lambda} (r^2 + z^2)^{\frac{1}{2}} J_0(2\pi/\lambda \cdot r \cdot \mu \sin \phi) (r^2 + z^2)^{-\frac{1}{2}} r dr \\ &= \lambda/2\pi (\mu^2 \sin^2 \phi - 1)^{-\frac{1}{2}} e^{-Z \frac{2\pi}{\lambda} (\mu^2 \sin^2 \phi - 1)^{\frac{1}{2}}} \end{aligned}$$

Substituting these values in the expression for the disturbance in the second medium when total reflexion is occurring, we find that the latter reduces to

$$A \cos \frac{2\pi}{\lambda} (Vt - r\mu \sin \phi) e^{-Z \frac{2\pi}{\lambda} (\mu^2 \sin^2 \phi - 1)^{\frac{1}{2}}}$$

Our investigation thus leads to precisely the same law of exponential decay as that derived from the Fresnel formulae for the superficial disturbance in the second medium, and the view that the latter is a diffraction-effect arising from the immediately contiguous part of the surface is thus fully substantiated.

In evaluating the diffraction integral, the area of the surface was taken as infinite, and we found that the case  $\mu \sin \phi = 1$  marks a point of discontinuity at which the phase of the secondary waves alters suddenly by quarter of a period, and their amplitude becomes very large. This circumstance and the form of the Fresnel zones drawn in Figs. 1 and 2 show that when the incidence is exactly at the critical angle, the finite extent of the surface cannot be ignored and must be taken into account for a more exact discussion. When however, the incidence is increased beyond the critical angle, the marginal portions of the area cease to be of importance in determining the observed effect at points not far from the surface. The further discussion of the phenomena at or very near the critical incidence and close to the surface on the basis of the integrals already given is a problem worthy of investigation which must however be deferred for the present.

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*The concluding portion of the paper and its summary  
appear on pages 330-331.*

# Experiments

on

## The Active Modification of Nitrogen

BY

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Ever since the discovery of active nitrogen by E. P. Lewis<sup>1</sup> many investigators including Lewis himself have attempted large number of experiments with a view to find out its real nature. Though a large number of its properties have come to light, the actual nature of the gas has, up to this time, remained obscure. The experimenters also seem to have suffered for want of any plausible theory to guide them in their work. Recently a number of theories have been advanced to explain the activities, chemical as well as spectral, and attempts have been made to fix up the physical nature of what is known as the active-modification of nitrogen. Unfortunately, however, sufficient experimental data are not available for testing the correctness of any one of these suggestions. Much experimental work seems to be necessary in the light of the new hypotheses; before it will be possible to say with certainty anything definite about the physical nature of active nitrogen and its mechanism of action.

The original discoverer Prof. E. P. Lewis himself gave no theory. Lord Rayleigh<sup>2</sup> was at one time in favour of the

<sup>1</sup> E. P. Lewis, *Astrophys J*, Vol 12, p 8, 1900

<sup>2</sup> R. J. Strutt, *Proc Roy Soc*, Vol 85, p 219, 1911; Vol. 86

idea that active-nitrogen stands in the same relation to ordinary nitrogen as ozone does to oxygen. But later on, he<sup>1</sup> seems to have given up that hypothesis.

In recent years Prof. M. N. Saha<sup>2</sup> and Mr. N. K. Sur have propounded the theory that active-nitrogen is simply a molecule of nitrogen loaded to an energy-content of 8-9 volts. When such active atoms come into collision with other atoms, they part with this energy by a collision of the second type as propounded by Klein<sup>3</sup> and Rosseland, and further worked out by Franck<sup>4</sup> and his students. The energy content of active-nitrogen was deduced from the excitation potential of the first primary band observed by Brandt<sup>5</sup> in the region 1200 to 1600 A.U., and of the lines of mercury which are excited when active nitrogen is made to act upon this element.

Prof. R. T. Birge,<sup>6</sup> from a study of the band spectra which were observed by Fowler<sup>7</sup> and Strutt when the glow of active-nitrogen was spectrographed, has given a similar explanation, but he thinks that the energy-content cannot be less than 11 to 12 volts.

More recently Sponer<sup>8</sup> has reviewed all the different theories and finds them all unsatisfactory. She is of opinion that active-nitrogen is simply atomic nitrogen, and cites in favour of her view certain experiments by Wood<sup>9</sup> and Bonhoeffer,<sup>10</sup> on the parallel properties of Hydrogen when activated by a discharge. Since this activated hydrogen shows the Balmer lines, it must be atomic, and since it

<sup>1</sup> R. J. Strutt, Proc. Roy. Soc., Vol. 87, p. 179, 1912

<sup>2</sup> M. N. Saha and N. K. Sur, Phil. Mag., Vol. 48, p. 421, 1924

<sup>3</sup> O. Klein and S. Rosseland, *Zs. f. Physik*, Vol. 4, p. 49, 1921.

<sup>4</sup> J. Franck, *Zs. f. Physik*, Vol. 9, p. 259, 1922; Vol. 11, p. 155, 1922.

Caro *Zs. f. Physik*, Vol. 10, p. 105 and p. 106, 1922

K. T. Compton, Jour. Opt. Soc. Am., Vol. 7, p. 955, 1923

<sup>5</sup> E. Brandt, *Zs. f. Physik*, Vol. 8, p. 32, 1922.

<sup>6</sup> R. T. Birge, Nature, Nov. 1, 1924.

<sup>7</sup> A. Fowler and R. J. Strutt, Proc. Roy. Soc., Vol. 85, p. 377, 1911.

<sup>8</sup> H. Sponer, *Zs. f. Physik*, Vol. 34, p. 622, 1925.

<sup>9</sup> R. W. Wood, Phil. Mag., Vol. 44, p. 538, 1922

<sup>10</sup> K. F. Bonhoeffer, *Zs. f. Phys. Chem.*, Vol. 113, p. 199, 1924

persists for a period of about one second, which is also the case with active-nitrogen, the analogy with activated hydrogen seems obvious. Sponer further argues that neither Saha and Sur nor Birge have advanced any definite hypothesis about the life of active-nitrogen beyond throwing out the suggestion that it is in some metastable state. We shall return to a discussion of Sponer's hypothesis later on.

Prof. M. N. Saha and Mr. N. K. Sur's paper contains many suggestions for differentiating amongst the prevalent theories. The writer has experimented on some of the effects suggested by the paper. In the apparatus that has been employed it is believed that considerable improvements have been made to warrant the hope that all obvious sources of error have been avoided, or at least very materially reduced.

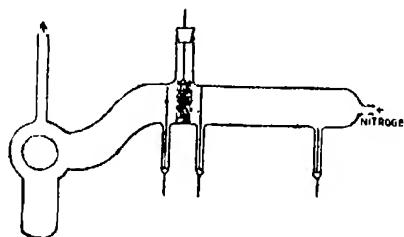


Fig. 1.

A diagram of the apparatus is given in fig. 1. The experimental tube consists of two parts, one in which the nitrogen is activated, the second in which the behaviour of activated nitrogen is observed. The discharge tube (D) has four side tubes  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  attached to it, with aluminium electrodes passing through  $E_1$ ,  $E_2$  and  $E_3$ . The electrodes through the side tubes  $E_2$ ,  $E_3$  which are about 3 cms. apart are kept protruding as much as possible inside the discharge tube. The side tube  $E_4$  on the other side of the discharge tube, is rather wide and allows a rubber stopper to be fitted to it. Through this passes a platinum wire with which is attached a very fine platinum wire-gauze occupying



the whole bore of the discharge tube and well in contact with the sides. The meshes of the wire-gauze are about a millimeter square. All these three electrodes  $E_2$ ,  $E_3$ ,  $E_4$  were separately connected to earth through water-pipes. The discharge tube is connected through a bend (B) about 12 cms. long, (which was made to prevent direct light of the discharge from coming and interfering with the observations) to the observation tube (O) which has four side tubes  $T_1$ ,  $T_2$ ,  $T_3$ ,  $T_4$  as shown in the sketch.  $T_3$ ,  $T_4$  being in the plane perpendicular to the plane of the paper are simply represented by a circle. All these side tubes with the exception of  $T_1$ , have about the same bore as the main-tube which is  $3/4$ " in diameter, and are four inches in length each.  $T_1$  is thinner and longer. While all the other tubes are open at both the ends  $T_2$  is closed at the lower. The two outer open ends of the tubes  $T_3$ ,  $T_4$  can either be closed by means of quartz windows, or rubber stoppers with electrodes passing through them as shown in fig. 2, which is a sketch of the observation tube as seen sideways. Though platinum electrodes have been used yet iron electrodes serve just as well. The whole tube is made entirely of pyrex glass.

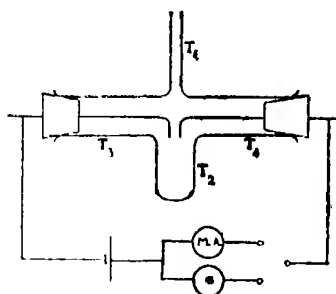


Fig. 2.

The side-tube  $T_2$  is capable of being completely surrounded by a tube-furnace and can therefore be heated to any desired degree. This tube furnace is very convenient and is

prepared in the following manner: G. No. 20 nichrome wire is wound round a silica tube of 1" internal diameter, round which screw threads are cut all along the length. This tube is put in another tube of thin sheet iron which fits it rather loosely, and the space inside the two is thoroughly packed with burnt asbestos powder. The whole is then given a covering of asbestos sheet. A brass cap closes one of the two open ends of the tube. With such a furnace any temperature up to a maximum of  $1000^{\circ}\text{C}$  inside can easily and quickly be obtained. A current of 2 amps gave a temperature of  $150^{\circ}\text{C}$ , while a temperature of  $600^{\circ}\text{C}$  was attained when 5.5 amps were flowing through it.

Activated nitrogen was prepared in the usual way. A glass bell-jar with a small iron-netting bag containing freshly cut chips of phosphorus hanging in it, was filled with commercial gas obtained from cylinders of nitrogen, and left overnight, after which it was ready for use. This nitrogen after passing through drying tubes and a capillary tube for regulating the supply entered the discharge tube where it was activated by means of a powerful condensed oscillatory discharge. The arrangement of electrical circuit for this is sketched in fig. 3. A spark gap (S) and a plate-

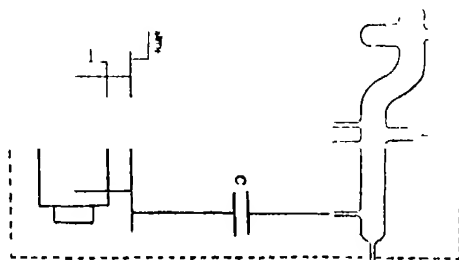


Fig 3.

glass condenser (C) of suitable capacity are put in parallel and series respectively with the secondary of an induction coil T and connected to the electrode  $E_1$ . The whole arrangement

including the coil and the discharge tube are put in a fine iron wire netting cage which is carefully earthed at several points and is shown by a broken line in the diagram. The activated nitrogen which is visible up to a distance of 10 or 12 inches, after streaming through the observation tube, is drawn out by a Gæde motor-driven pump.

With this apparatus most of the experiments conducted by Lord Rayleigh were repeated and confirmed. It is remarkable that the phenomenon of after-glow is observable only when the *discharge is oscillatory* and stops entirely when the discharge is silent.

Very minute quantities of oxygen proved fatal to the production of active-nitrogen. Cupric oxide also completely extinguishes the glow. A fine clean piece of platinoid wire was inserted in the glow and it was noticed that the glow abruptly stopped. This was attributed to the presence of oxide of copper in platinoid which we have seen has such destructive effects upon the glow.

Active-nitrogen dies down when led through a capillary tube. It is not believed that the tube was in any way dirty. The glass alone could have effected the glow in this way. But the matter was not investigated further.

In experimenting with iodine, the apparatus shown in fig. 1 was employed. The iodine was put in a small platinum cylinder and hung by means of a platinum wire attached to the rubber cork in the tube  $T_1$ . The electric furnace was very slightly heated. As the active nitrogen came in contact with iodine vapour a blue glow became visible.

In experimenting with mercury, a few drops of clean mercury were put into the side-tube  $T_2$  and the temperature raised to  $150^{\circ}\text{C}$ , which gave a pressure of mercury of about 2.5 m.m., which was enough considering the vacuum produced

by the pump. The vapour on coming in contact with the active-nitrogen gave a very bright bluish glow. There was a dividing surface between the two glows, which was very prominent. The luminosity entirely disappeared when the input of nitrogen was stopped and ordinary air put in its place, the discharge running all the while. Repeated experiments left no doubt that it was activated-nitrogen alone which was responsible for the change in the behaviour of mercury atoms. Two iron electrodes as shown in fig. 2 were immersed in the mercury glow and put in series with a couple of Leclanche cells, and a microammeter (M.A.) and a Wilberforce Galvanometer (G) put in such a way that any of them could be used at will. No ionisation current was observed, the pointers remaining perfectly steady.

In sodium experiments it was found that the earlier types of tubes where activated nitrogen streamed perpendicular to the path of the jet of sodium atoms were unsuitable. It was noticed that Na atoms were prevented from coming up and mixing freely with the active-nitrogen. The tube was therefore modified to the form shown in fig. 4.

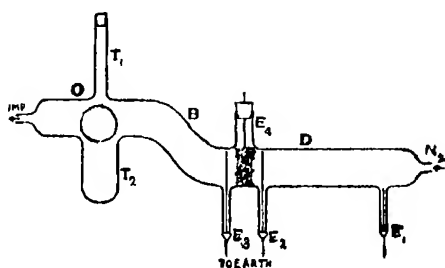


Fig. 4.

The main side-tube has been dispensed with, and in its place the nitrogen is sucked through  $T_1$ . This modification made it possible for the free mixing up of active-nitrogen with Na atoms. Under these conditions intense yellow light enveloped the electrodes. The experiment for finding if any

ionisation is produced was attempted and the following observations were recorded:—

Area of electrodes	=	·7 sq. cms.
Distance between electrodes	=	3 mm.
Current passing when the electrodes are immersed in active nitrogen only	=	no current.
Current passing when the electrodes are immersed in Na vapour only	=	no current.
Current when the electrodes are immersed in Na vapour activated by glow	=	2·5 mic amps.
Potential applied	=	3 Volts.

The sodium vapour is thus found to be definitely ionised as was predicted in Saha <sup>1</sup> and Sur's paper.

### DISCUSSION.

It seems to be definitely established that active-nitrogen carries no free charge or any charged particle of  $N_2$ . In the present arrangement special care has been taken to remove all free ions by putting a platinum gauze in the path of the active nitrogen and connecting it to earth. The electrodes were also shielded adequately from the direct induction effects of the terminals of induction coil. Under these conditions not a trace of current was established between the two plates. It was however observed that when the screening was inadequate, tiny sparks passed between the two plates, and transient and irregular currents were established between the electrodes. The current observed by E. P. Lewis <sup>2</sup> and attributed by him to the presence of free electrons in the glow, is probably due to insufficient shielding of the induction coil. That no charged

<sup>1</sup> M. N. Saha and N. K. Sur, *loc.cit*

<sup>2</sup> E. P. Lewis, *Nature*, Vol. 111, p. 599, 1923.

particles are present is also proved by the absence of negative bands in the spectra photographed by Fowler<sup>1</sup> and Lord Rayleigh.

The present work confirms in a general way the observations of Lord Rayleigh, and proves that Na is ionised when acted upon by active-nitrogen as predicted by Saha and Sur. This experiment of course does not decide between the theories of Saha and Sponer. As it stands, Sponer's theory is largely based upon the analogy of active-nitrogen with active-hydrogen. But it seems that Sponer has not put the correct interpretation on Wood's experiments. These prove that active-hydrogen atom is not the normal H-atom but an H-atom in which the electron is lifted to a higher orbit. The active-hydrogen is therefore an atom of hydrogen loaded to an energy content of at least 11 volts. If Sponer's theory were correct, by analogy we can conclude that active-nitrogen atom is not normal, but that in this case too, the electron is raised to higher quantum orbits. This point can only be answered by examining the spectrum of active-nitrogen. Fowler and Lord Rayleigh have recorded that the spectrum consists of 1st, 2nd, 3rd and 4th positive bands. They have not recorded any lines due to atomic nitrogen. It might be argued that they did not look for the lines of atomic nitrogen, as Kiess<sup>2</sup> has recorded in a recent paper that the chief lines of atomic nitrogen lie either in the Schumann region or in the far infra-red. There are no strong lines in the visible range at all, so that when  $N_2$  is excited by putting gradually increasing stimulus through it and the observation is confined within the usual range  $\lambda$  2300- $\lambda$ 7000 A. U., we get nothing intermediate between the band spectra or lines emitted by ionised nitrogen. To establish the presence of atomic nitrogen we must work either in the

<sup>1</sup> Fowler and Strutt, *loc-cit*

<sup>2</sup> C. C. Kiess, Jour Opt. Soc. Am., Vol 11, p. 1, 1925.

Schumann region or in the extreme infra-red. The lines which lie in the visible range belong to a very subordinate combination and according to Saha<sup>1</sup> they might be missing under the ordinary conditions of experiments. Active nitrogen seems to contain no  $N^+$  atoms, for the characteristic line of  $N^+$ ,  $\lambda 3995$  is definitely absent.

Experiments to test Sponer's hypothesis are in progress.

The writer wishes to express his grateful thanks to Prof. M. N. Saha for his kind interest in and advice during the progress of these experiments.

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<sup>1</sup> M. N. Saha, Jour Ind Chem Soc, p 49, 1925

# On the Pressure exerted by an Elastic Hammer impinging on a Pianoforte String.

BY

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## INTRODUCTION.

The following discussion is a continuation of the work published in the Proceedings of the Indian Association for the Cultivation of Science (Vol. VII, Parts I and II, 1921). In the paper last cited, the investigation was confined to the case of a rigid hammer, whereas the present one is concerned with the more general case of the elastic hammer. The same method, as was used in the previous work, has been adopted here, *viz*, that of successive functional solutions of the wave-equation for a stretched string.



FIG. 1

Let AOB be a stretched string, of which the point O is struck by an elastic hammer of pointed shape, so that the area of contact is zero. Consider the state of affairs when the centre of gravity of the hammer has had a displacement  $\zeta$  from  $G^1$  to  $G$ . The compression is denoted by  $u$  and the displacement of the string at O and any two points on the parts OA, OB respectively by  $y_0, y, y_1$ , as shown in Fig. 1.



OA is taken as the positive direction of the axis of  $x$ . If  $T$  be the tension,  $m$  the mass of the hammer and  $c$  the wave velocity along the string, the equations of motion of the string and the hammer are respectively:—

$$\frac{\partial^2 y}{\partial t^2} = c^2 \frac{\partial^2 y}{\partial x^2} \quad \dots \quad (I)$$

$$\text{and} \quad m \frac{d^2 \zeta}{dt^2} = T \left( -\frac{\partial y_1}{\partial x} + \frac{\partial y_2}{\partial x} \right)_{x=0}$$

$$= \text{pressure of impact.} \quad \dots \quad (II)$$

Now if the area of contact be finite and constant, then within the limits of elasticity this pressure of impact may be taken to be proportional to the compression  $u$  and equals  $Eu$ , say, where  $E$  is a constant. It is evident from the diagram that the displacement  $\zeta$  of the hammer = the displacement  $y_0$  + the compression  $u$ .

$$\zeta = y_0 + u \quad \dots \quad (1)$$

Thus the equation (II) becomes

$$m \frac{d^2 y_0}{dt^2} + m \frac{d^2 u}{dt^2} = T \left( -\frac{\partial y_1}{\partial x} + \frac{\partial y_2}{\partial x} \right)_{x=0} = -Eu \quad \dots \quad (III)$$

The solution of (I) takes the functional form

$$\left. \begin{aligned} y_1 &= f_1(ct + t) \\ y_2 &= f_1(ct - t) \\ y_0 &= f_1(ct) \end{aligned} \right\} \quad \dots \quad (IV)$$

Substituting these in (III) we get:—

$$mc^2 f_1''(ct) + m \frac{d^2 u}{dt^2} = -2T f_1'(ct) = -Eu \quad \dots \quad (2)$$

$$\text{which gives } u = -\frac{2T}{E} f_1'(ct) = \lambda f_1'(ct) \quad \dots \quad (3)$$

$$\text{where} \quad \lambda = \frac{2T}{E} \quad \dots \quad (4)$$

Substituting the value of  $u$  from (3) in (2) we get:—

$$mc^2 \lambda f_1'''(ct) + mc^2 f_1''(ct) + E \lambda f_1'(ct) = 0$$

$$\text{or} \quad f_1'''(ct) + \frac{1}{\lambda} f_1''(ct) + \frac{E}{mc^2} f_1'(ct) = 0 \quad \dots \text{ (V)}$$

$$\text{If we write } z = ct \text{ and } \phi_1(z) = f_1'(z) \quad \dots \text{ (5)}$$

then (V) becomes:—

$$\frac{d^2 \phi_1}{dz^2} + \frac{1}{\lambda} \frac{d\phi_1}{dz} + \frac{E}{mc^2} \phi_1 = 0 \quad \dots \text{ (VI)}$$

The solution of this equation is

$$\phi_1(z) = A_1 e^{\alpha z} + B_1 e^{\beta z} \quad \dots \text{ (6)}$$

where  $\alpha, \beta$  are the roots of  $x^2 + \frac{x}{\lambda} + \frac{E}{mc^2} = 0$ ,

and  $A_1, B_1$  are arbitrary constants.

As usual, the constants  $A_1, B_1$  are to be determined by the initial conditions. Let the impinging velocity of the hammer =  $V$ ; the initial value of the compression  $u$  is also zero. Thus, when  $t = 0, u = 0$ ; which gives

$$u = \lambda f_1'(ct) \Big|_{t=0} = 0$$

$$\text{i.e.,} \quad A_1 + B_1 = 0, \text{ or } A_1 = -B_1 \quad \dots \text{ (7)}$$

$$\text{And } \frac{d\xi}{dt} = V = \left( \frac{dy_0}{dt} + \frac{du}{dt} \right) \Big|_{t=0}$$

$$\begin{aligned} \text{i.e.,} \quad V &= c f_1'(ct) \Big|_{t=0} + \lambda c f_1''(ct) \Big|_{t=0} \\ &= \lambda c (A_1 \alpha + B_1 \beta) = \lambda c A_1 (\alpha - \beta). \end{aligned}$$

$$\text{Hence } A_1 = -B_1 = \frac{V}{c\lambda(\alpha - \beta)} \quad \dots \text{ (8)}$$

Now these solutions describe the motion of the hammer until the wave starting from  $O$  is reflected from the near end  $A$  of the string and again reaches the hammer at  $O$ . At that instant fresh waves are excited at  $O$ , while the already existing waves pass on, as has been assumed in the previous work. Thus the solutions just obtained hold good only within a

period or epoch defined by  $0 < ct < 2a$  where  $OA = a$ . As I have shown in my first paper, the whole course of the motion has to be divided into a series of epochs of magnitude  $2a/c$ , and the successive solutions are different from each other. So we proceed to study the motion in the order of successive epochs. It is assumed here also that the remote end B of the string is so much further away from O than A, that the impact ceases before the first reflection from B reaches O. It will be seen later on that this limitation is only a temporary one and can be easily removed.

### §1.

#### Successive Solutions.

First Epoch ( $0 < ct < 2a$ ):—

Here we have,

$$y_1 = f_1(ct + x)$$

$$y_2 = f_1(ct - x)$$

$$y_0 = f_1(ct)$$

$$\text{where } f_1'(ct) = \frac{V}{c\lambda(a - \beta)} \left( e^{act} - e^{\beta ct} \right) \quad \dots \quad (9)$$

Second Epoch ( $2a < ct < 4a$ ) —

As in the paper cited we assume that

$$\left. \begin{aligned} y_1 &= f_1(ct + x) + f_2(ct + x) - f_1(ct + x - 2a) \\ y_2 &= f_1(ct - x) + f_2(ct - x) - f_1(ct + x - 2a) \\ y_0 &= f_1(ct) + f_2(ct) - f_1(ct - 2a) \end{aligned} \right\} \quad \dots \quad (10)$$

The function  $f_1(ct \pm x)$  represents the original wave,  $f_2(ct \pm x)$  the freshly excited wave, of which the form is yet to be found, and  $-f_1(ct + x - 2a)$ , the wave reflected from the end A.

Substituting the values (10) in (III) we get

$$u = \frac{2T}{E} \{f_1'(ct) + f_2'(ct)\}, \quad \dots \quad (11)$$

which being again substituted in the same, gives, after simplification with the help of (V) :—

$$f_1'''(ct) + \frac{1}{\lambda} f_1''(ct) + \frac{E}{mc^2} f_1'(ct) = \frac{1}{\lambda} f_1''(ct - 2a) \quad (\text{VII})$$

If we now write  $z = ct$  and  $\phi_1(z) = f_1(z)$ , then (VII) and (9) give :—

$$\begin{aligned} \frac{d^3 \phi_1}{dz^3} + \frac{1}{\lambda} \frac{d\phi_1}{dz} + \frac{E}{mc^2} \phi_1 &= \frac{1}{\lambda} \phi_1'(z - 2a) \quad \dots \quad (\text{IX}) \\ &= \frac{V}{c\lambda^2(\alpha - \beta)} \{ \alpha e^{\alpha(z-2a)} - \beta e^{\beta(z-2a)} \} \end{aligned}$$

If we write  $z' = z - 2a$  then

$$\frac{d}{dz} = \frac{d}{dz'}$$

and the above written equation reduces to :—

$$\frac{d^3 \phi_1}{dz'^3} + \frac{1}{\lambda} \frac{d\phi_1}{dz'} + \frac{E}{mc^2} \phi_1 = \frac{A_1}{\lambda} (\alpha e^{\alpha z'} - \beta e^{\beta z'})$$

The complete integral of this is

$$\phi_1(z') = A_1 e^{\alpha z'} + B_1 e^{\beta z'} + \frac{1}{(D - \alpha)(D - \beta)} \cdot \frac{A_1}{\lambda} (\alpha e^{\alpha z'} - \beta e^{\beta z'})$$

where  $A_1, B_1$  are arbitrary constants and  $D \equiv \frac{d}{dz'}$

This easily reduces to :—

$$\phi_1 = A_1 e^{\alpha z'} + B_1 e^{\beta z'} + \frac{V z'}{c\lambda^2(\alpha - \beta)} \{ \alpha e^{\alpha z'} + \beta e^{\beta z'} \} \quad \dots \quad (12)$$

We next discuss the initial conditions. In the case of the rigid hammer, the pressure of impact is an impulsive force at the moment it just touches the string, because it instantaneously imparts a velocity  $V$  to the part of the string it comes in contact with. In the case of the elastic hammer however,

the pressure is developed slowly, as the otherwise impulsive nature of contact-pressure is deadened by the elasticity of the hammer, so that the string is gradually set in motion. Hence the reflected pulse on reaching G will not cause any discontinuous change in the velocity of either the string or the hammer. We thus assume that

$$\frac{dy_0}{dt} \quad \text{and} \quad \frac{d\zeta}{dt}$$

are both continuous at the instant of impact  $ct = 2a$ .

$$\text{Thus} \quad \frac{dy_0}{dt} = \frac{1}{c} f_1'(ct)_{ct=2a} \quad [\text{for first epoch}]$$

$$= \frac{1}{c} [f_1'(ct) + f_2'(ct) - f_1'(ct-2a)]_{ct=2a} \quad [\text{for second epoch}]$$

$$\text{or} \quad f_2'(2a) = f_1'(0) = 0 \quad \dots (13)$$

$$\text{i.e.,} \quad A_2 + B_2 = 0, \quad \text{or} \quad A_2 = -B_2 \quad \dots (14)$$

Similarly, the continuity of  $\frac{d\zeta}{dt}$  gives

$$f_1''(2a) = f_1''(2a) + f_2''(2a)$$

$$\text{or} \quad f_2''(2a) = 0. \quad \dots (15)$$

$$\text{i.e.,} \quad \alpha A_2 + \beta B_2 + \frac{V}{c\lambda^2(\alpha - \beta)^2} (\alpha + \beta) = 0$$

$$\text{or} \quad A_2 = -B_2 = + \frac{V}{c\lambda^2(\alpha - \beta)^2} \quad \dots (16)$$

$$\text{since} \quad \frac{1}{\lambda} = -(\alpha + \beta)$$

Thus the result (14) can be written:—

$$\begin{aligned} \phi_2(s) = \frac{V}{c\lambda^2(\alpha - \beta)^2} & \left[ e^{\alpha z'} \{1 + \alpha\lambda(\alpha - \beta)z'\} \right. \\ & \left. + e^{\beta z'} \{1 + \beta\lambda(\alpha - \beta)z'\} \right] \quad \dots (17) \end{aligned}$$

where  $z' = s - 2a$ .

Third Epoch ( $4a < ct < 6a$ ) :—

A fresh disturbance  $f_3(ct \pm x)$  will now arise, and the reflected wave  $-f_2(ct + x - 2a)$  will arrive at 0. Hence the functional forms of  $y_1, y_2$  have to be altered by adding to the values corresponding to the second epoch the waves  $f_3(ct \pm x)$  and  $-f_2(ct + x - 2a)$ . An expression for the compression  $u$  is derived by substituting these, as before in (III). Thus,

$$u = \frac{2T}{E} \left[ f'_1(ct) + f'_2(ct) + f'_3(ct) \right] \quad \dots \quad (18)$$

$$\text{If we write } \phi_3(z) = f'_3(z) \quad \dots \quad (19)$$

the differential equation for  $\phi_3$  becomes

$$\frac{d^2 \phi_3}{dz^2} + \frac{1}{\lambda} \frac{d\phi_3}{dz} + \frac{E}{mc^2} \phi_3 = \frac{1}{\lambda} \phi'_1(z - 2a) \quad \dots \quad (X)$$

where  $z = ct$ .

It is easily seen that the integral of this equation will be of the form

$$\phi_3(z) = e^{\alpha z'} (a_0 + a_1 z' + a_2 z'^2) + e^{\beta z'} (b_0 + b_1 z' + b_2 z'^2) \quad \dots \quad (18)$$

$$\text{where } z' = z - 4a \quad \text{Initial conditions give } \phi_3(4a) = \phi'_3(4a) = 0 \dots \quad (19)$$

Before deriving the coefficients  $a_0, a_1$ , etc., directly, we proceed to consider the nature of functional forms of the wave-motion during the succeeding epochs.

Succeeding Epochs :—

During the fourth epoch a new wave  $f_4(ct \pm x)$  will arise and the reflection  $-f_3(ct + x - 2a)$  will reach the hammer. These have to be added to the preceding disturbances.

The compression will be

$$u = \frac{2T}{E} \sum_1^4 f'_r(ct) \quad \dots \quad (20)$$

$$\text{If } \phi_4(z) = f'_4(z), \quad \dots \quad (21)$$

then a study of the results (IX) and (X) will show that the differential equation for  $\phi_1$  will be

$$\frac{d^2 \phi_1}{dz^2} + \frac{1}{\lambda} \frac{d\phi_1}{dz} + \frac{E}{mc^2} \phi_1 = \frac{1}{\lambda} \phi'_1(z-2a) \quad \dots \text{ (XI)}$$

A study of the results (17) and (18) will show that the general integral will be of the form

$$\begin{aligned} \phi_1(z) = e^{\alpha z} (a_0 + a_1 z + a_2 z^2 + a_3 z^3) \\ + e^{\beta z} (b_0 + b_1 z + b_2 z^2 + b_3 z^3) \quad \dots \text{ (22)} \end{aligned}$$

$$\text{where } z_3 = z - 3.2a \quad \dots \text{ (24)}$$

Since the method is perfectly general, it will be seen that at the  $(n+1)$ th epoch characterised by  $n \cdot 2a < ct < (n+1) \cdot 2a$ , the wave-motion will be represented by

$$[y_1, y_2] = \sum_1^{n+1} f_r(ct \pm x) - \sum_1^n f_r(ct + x - 2a) \quad \dots \text{ (25)}$$

$$\text{and } u = \frac{2T}{E} \sum_1^{n+1} f'_r(ct) \quad \dots \text{ (26)}$$

$$\text{If } \phi_r(z) = f'_r(z), \quad \dots \text{ (27)}$$

$$\text{and } z_n = z - n \cdot 2a, \quad \dots \text{ (28)}$$

the wave-equation will be of the form

$$\frac{d^2 \phi_{n+1}}{dz^2} + \frac{1}{\lambda} \frac{d\phi_{n+1}}{dz} + \frac{E}{mc^2} \phi_{n+1} = \frac{1}{\lambda} \phi'_{n+1}(z - n \cdot 2a) \quad \dots \text{ (XII)}$$

And the form of  $\phi_{n+1}$  will be given by

$$\begin{aligned} \phi_{n+1}(z) = e^{\alpha z} ({}_{n+1}a_0 + {}_{n+1}a_1 z_n \dots {}_{n+1}a_r z_n^r + \dots {}_{n+1}a_n z_n^n) \\ + e^{\beta z_n} ({}_{n+1}b_0 + {}_{n+1}b_1 z_n + \dots {}_{n+1}b_r z_n^r + \dots {}_{n+1}b_n z_n^n) \quad \dots \text{ (29)} \end{aligned}$$

$\phi_n(z)$  is derived by writing  $n$  for  $n+1$  in (29).

Substituting these in (XII) and equating the co-efficients of  $e^{az} z^r$  and  $e^{\beta z} z^r$  from both sides, and simplifying the result obtained with the help of the fact that  $\alpha, \beta$  are roots of

$$x^2 + x/\lambda + E/mc^2 = 0$$

we get

$$\begin{aligned} (\alpha - \beta)_{n+1} a_{r+1} + (r+2)_{n+1} a_{r+2} \\ = \frac{1}{\lambda} \left( {}_n a_{r+1} + \frac{{}_n a_r}{r+1} \cdot \alpha \right) \end{aligned} \quad \dots (30)$$

$$\text{and } (\beta - \alpha)_{n+1} b_{r+1} + (r+2)_{n+1} b_{r+2}$$

$$= \frac{1}{\lambda} \left( {}_n b_{r+1} + \frac{{}_n b_r}{r+1} \beta \right) \quad \dots (31)$$

The continuity of  $\frac{dy}{dt}$  and  $\frac{du}{dt}$  at the instant  $ct = 2na$ , gives

$$\phi_{n+1}(2na) = \phi'_{n+1}(2na) = 0 \quad \dots (32)$$

$$\text{or } {}_{n+1} a_0 + {}_{n+1} b_0 = 0 \quad \dots (33)$$

$$\text{and } {}_{n+1} a_0 \cdot \alpha + {}_{n+1} a_1 + {}_{n+1} b_0 \cdot \beta + {}_{n+1} b_1 = 0 \quad \dots (34)$$

The results (30), (31), (33) and (34) will enable us to determine the co-efficients  ${}_n a_r, {}_n b_r$ , for all values of  $n$  and  $r$ . We have to remember that  ${}_n a_r, {}_n b_r$ , are zero for values of  $r$  greater than  $n-1$ .

First put  $r = n-1$  in (30). Then

$$(\alpha - \beta)_{n+1} a_n = \frac{{}_n a_{n-1}}{n} \cdot \frac{\alpha}{\lambda}$$

$$\text{Similarly } (\alpha - \beta)_n a_{n-1} = \frac{{}_{n-1} a_{n-2}}{n-1} \cdot \frac{\alpha}{\lambda}$$

$$\text{Thus we get } {}_{n+1} a_n = \frac{{}_1 a_0}{(\alpha - \beta)^n} \cdot \frac{1}{\lambda^n} \cdot \frac{\alpha^n}{\lambda^n} \quad \dots (35)$$



Next put  $r=n-2$  in (30). Then

$$(a-\beta)_{n+1}a_{n-1} = -n_{n+1}a_n + \frac{n a_{n-2}}{n-1} \cdot \frac{a}{\lambda} + \frac{n a_{n-2}}{\lambda}.$$

If we utilise the result (35), this becomes:—

$$_{n+1}a_{n-1} = - \left( \frac{_1a_0}{(a-\beta)^{n+1}} \cdot \frac{1}{n-1} \cdot \frac{a^{n-1}\beta}{\lambda^n} + \frac{_{n-1}a_{n-2}}{(n-1)\lambda} \cdot \frac{a}{a-\beta} \right)$$

Similarly,

$$\left. \begin{aligned} _na_{n-2} &= - \left( \frac{_1a_0}{(a-\beta)^n} \cdot \frac{1}{n-2} \cdot \frac{a^{n-2}\beta}{\lambda^{n-1}} + \frac{_{n-2}a_{n-3}}{(n-2)\lambda} \cdot \frac{a}{a-\beta} \right) \\ _{n-1}a_{n-3} &= - \left( \frac{_1a_0}{(a-\beta)^{n-1}} \cdot \frac{1}{n-3} \cdot \frac{a^{n-3}\beta}{\lambda^{n-2}} + \frac{_{n-3}a_{n-4}}{(n-3)\lambda} \cdot \frac{a}{a-\beta} \right) \\ &\dots \dots \dots \\ _1a_1 &= - \left( \frac{_1a_0}{(a-\beta)^2} \cdot \frac{1}{1} \cdot \frac{a\beta}{\lambda^2} + \frac{_1a_0}{\lambda} \cdot \frac{a}{a-\beta} \right) \end{aligned} \right\} \dots (36)$$

Hence, multiplying the second equation by

$$\frac{1}{n-1} \cdot \frac{a}{a-\beta}$$

the third equation by

$$\frac{1}{(n-1)(n-2)} \cdot \frac{a}{(a-\beta)^2}$$

and so on, and adding up, we get

$$_{n+1}a_{n-1} = - \left( \frac{_1a_0}{(a-\beta)^{n+1}} \cdot \frac{1}{n-2} \cdot \frac{a^{n-1}\beta}{\lambda^n} + \frac{_1a_0}{(a-\beta)^{n-1}} \cdot \frac{1}{n-1} \cdot \frac{a^{n-1}}{\lambda^{n-1}} \right) \dots (37)$$

Before proceeding with the general calculation of these co-efficients any further we proceed now to calculate these for the first few epochs.

We have from (29),

$$\left. \begin{aligned} \phi_1(z) &= {}_1a_0 \cdot e^{az} + {}_1b_0 e^{\beta z} \dots \dots \dots \\ \text{and } \phi_2(z) &= e^{az} \cdot ({}_2a_0 + {}_2a_1 z_1) + e^{\beta z} \cdot ({}_2b_0 + {}_2b_1 z_1) \dots \dots \dots \end{aligned} \right\} \dots (38)$$

Comparing (38) with (9) and (17) we get

$$,a_0 = -,b_0 = \frac{V}{c} \cdot \frac{1}{\lambda(a-\beta)} \quad \dots (39)$$

$$,a_0 = -,b_0 = \frac{V}{c} \cdot \frac{1}{\lambda^2(a-\beta)^2} \quad \dots (40)$$

$$\text{and } ,a_1 = \frac{V}{c} \cdot \frac{a}{\lambda^2(a-\beta)^2} \quad \dots (41)$$

$$,b_1 = \frac{V}{c} \cdot \frac{\beta}{\lambda^2(a-\beta)^2} \quad \dots (42)$$

It is evident that by putting  $r=n-1$ ,  $n-2$ , etc., in succession in equation (30), the co-efficients of the  $(n+1)$ th epoch can all be calculated [use must also be made of (31), (33) and (34)], provided that we know their values at the  $n$ th epoch. We have already found the values for the 1st and 2nd epochs, hence the values for the subsequent epochs can be calculated.

If we have to derive a general expression for  $,a_r$  by the method indicated in (36), the process becomes too laborious and the result too unwieldy for numerical evaluation. Hence we shall simplify the calculation by considering special cases. If the elasticity of the hammer is very large, some simplifications follow at once. We have

$$[a, \beta] = \frac{-\frac{1}{\lambda} \pm \sqrt{\frac{1}{\lambda^2} - \frac{4E}{mc^2}}}{2}$$

$$\text{Now } \lambda = \frac{2T}{E} \quad \text{and } c^2 = \frac{T}{\rho}$$

where  $\rho$  = line-density of string.

Hence if  $E$  is very large compared to  $T$ , then, the roots become

$$-\frac{2\rho}{m} \quad \text{and} \quad -\frac{E}{2T},$$

approximately,

$$\text{i.e. } \alpha = -\frac{2\rho}{m} \text{ and } \beta = -\frac{E}{2T} \quad \dots (43)$$

$$\text{Then } -\frac{1}{\lambda} = -(\alpha + \beta) = -\beta$$

approximately if we neglect  $\alpha$  in comparison with  $\beta$ ;

$$\text{or } \beta\lambda = -1. \quad \dots (44)$$

Hence the results (39) to (42) become

$$\left. \begin{aligned} {}_1a_0 &= -{}_1b_0 = \frac{V}{c} \\ {}_2a_0 &= -{}_2b_0 = \frac{V}{c} \\ {}_3a_1 &= \frac{V}{c}{}_3a, {}_3b_1 = \frac{V}{c}\beta \end{aligned} \right\} \quad \dots (45)$$

From (35) and (37) we get

$${}_{n+1}a_n = \frac{V}{c} \cdot \frac{a^n}{\lfloor n} \quad \dots (46)$$

$${}_{n+1}a_{n-1} = \frac{V}{c} \cdot \frac{n a^{n-1}}{\lfloor n-1} \quad \dots (47)$$

To calculate

$${}_{n+1}a_{n-2}$$

we put  $r=n+3$  in (30). We easily get

$${}_{n+1}a_{n-2} = \frac{V}{c} \cdot \frac{n-1}{\lfloor n-2} \cdot a^{n-1} + \frac{{}_2a_{n-1}}{n-2} \cdot a.$$

Applying the process indicated in (36) we get

$${}_{n+1}a_{n-2} = \frac{V}{c} \cdot \frac{1}{\lfloor n-2} \cdot a^{n-1} [1+2+3\dots n-1]$$

$$= \frac{V}{c} \cdot \frac{1}{\lfloor n-2} \cdot \frac{n(n-1)}{\lfloor 2} \cdot a^{n-1} \quad \dots (48)$$

In the same manner

$$\begin{aligned} a_{n-1} a_{n-2} &= \frac{V}{c} \cdot \frac{1}{L^{n-3}} \cdot \frac{n(n-1)(n-2)}{L^3} a^{n-3} \\ &= \frac{V}{c} \cdot \frac{1}{L^{n-3}} \cdot {}^nC_3 \cdot a^{n-3} \end{aligned} \quad \dots (48)$$

Generally,

$$a_{n+1} a_r = \frac{V}{c} \cdot \frac{1}{L^r} \cdot {}^nC_r \cdot a^r \quad \dots (49)$$

Precisely in the same manner we get

$$a_{n+1} b_r = -\frac{V}{c} \cdot \frac{\beta^r}{(-1)^r} \cdot \frac{1}{L^r} \quad \dots (50)$$

$$\begin{aligned} \text{Thus } \phi_{n+1}(z) &= e^{az_n} \sum_{r=0}^{r=n} a_{n+1} a_r z_n^r + e^{\beta z_n} \sum_{r=0}^{r=n} a_{n+1} b_r z_n^r \\ &= \frac{V}{c} \left[ e^{az_n} \left( 1 + na z_n + \frac{n(n-1)}{L^2} \cdot \frac{a^2 z_n^2}{L^2} + \frac{n(n-1)(n-2)}{L^2} \cdot \frac{a^3 z_n^3}{L^2} + \dots \right. \right. \\ &\quad \left. \left. \dots \frac{na^{n-1} z_n^{n-1}}{L^{n-1}} + \frac{a^n z_n^n}{L^n} \right) \right. \\ &\quad \left. e^{\beta z_n} \left( 1 - \beta z_n + \frac{\beta^2}{L^2} z_n^2 - \frac{\beta^3}{L^3} z_n^3 \dots (-)^n \frac{\beta^n}{L^n} z_n^n \right) \right] \quad \dots (51) \end{aligned}$$

If we denote the compression during this epoch by  $u_{n+1}$ , then from the result (26) we have

$$\begin{aligned} u_{n+1} &= \frac{2T}{E} \sum_1^{n+1} f_r'(ct) \\ &= \frac{2T}{E} \sum_1^{n+1} \phi_r(ct) \end{aligned}$$

$\therefore$  Hence the pressure of impact  $F_{n+1}$  during the same epoch is given by

$$F_{n+1} = E u_{n+1} = 2T \sum_1^{n+1} \phi_r(ct). \quad \dots (52)$$

For instance, the pressure at the first three epochs are

$$\begin{aligned}
 F_1 &= 2T \cdot \frac{V}{c} \left[ e^{\alpha x_1} - e^{\beta x_1} \right] \\
 &= \frac{2TVc\rho}{T} \left[ e^{\alpha ct} - e^{\beta ct} \right] \\
 &= 2\rho Vc \left[ e^{\alpha ct} - e^{\beta ct} \right] \quad \dots \quad (53)
 \end{aligned}$$

$$\begin{aligned}
 F_2 &= 2\rho Vc \left[ e^{\alpha ct} + e^{\alpha(ct-2a)} \left\{ 1 + \alpha(ct-2a) \right\} \right. \\
 &\quad \left. - e^{\beta ct} - e^{\beta(ct-2a)} \left\{ 1 - \beta(ct-2a) \right\} \right] \quad \dots \quad (54)
 \end{aligned}$$

$$\begin{aligned}
 F_3 &= 2\rho Vc \left[ e^{\alpha ct} + e^{\alpha(ct-2a)} \left\{ 1 + \alpha(ct-2a) \right\} \right. \\
 &\quad \left. + e^{\alpha(ct-4a)} \left\{ 1 + 2\alpha(ct-4a) + \frac{\alpha^2}{2} (ct-4a)^2 \right\} \right. \\
 &\quad \left. - e^{\beta ct} - e^{\beta(ct-2a)} \left\{ 1 - \beta(ct-2a) \right\} \right. \\
 &\quad \left. - e^{\beta(ct-4a)} \left\{ 1 - \beta(ct-4a) + \frac{\beta^2}{2} (ct-4a)^2 \right\} \right] \quad \dots \quad (55)
 \end{aligned}$$

respectively, and so on.

Before undertaking a general interpretation of these results, we shall first consider a few special cases of importance.

## § 2. RIGID HAMMER.

A fair approximation to the rigid hammer can be made by regarding the elasticity-constant  $E$  as indefinitely large. Then  $\alpha, \beta$  are given by (43) as follows :

$$\alpha = -\frac{2\rho}{m} \quad \text{and} \quad \beta = -\frac{E}{2T}$$

Now since the limiting value of  $x^n e^{-x}$  can be shown to be zero for  $x = \infty$ , so long as  $n$  is finite, the terms involving

$\beta$  in the expression for the pressures  $F_1, F_2$ , etc., are all zero. Hence these reduce to

$$F_1 = 2\rho Vc e^{act} \quad \dots \quad (56)$$

$$F_2 = 2\rho Vc \left[ e^{act} + e^{a(ct-2a)} \left\{ 1 + a(ct-2a) \right\} \right] \quad \dots \quad (57)$$

and so on.

It will be seen that these expressions are identical with those derived in my previous paper.

### § 3. SOFT HAMMER.

We have seen that  $\alpha, \beta$  are the values of the expression :—

$$-\frac{E}{2T} \pm \sqrt{\frac{E^2}{4T^2} - \frac{4\rho E}{mT}}$$

If the expression under the radical be negative, we can write it as a complex quantity of the form  $\xi + \eta i$ . The condition that such may be the case is that

$$\frac{16\rho}{m} > \frac{E}{T} \quad \dots \quad (58)$$

Since the line-density  $\rho$  is generally small compared with the mass  $m$  of the hammer, the elasticity-constant  $E$  is also small compared with the tension  $T$  of the string. In other words, the hammer is light and soft.

$$\begin{array}{ll} \text{Thus we have} & \alpha = \xi + \eta i \\ \text{and} & \beta = \xi - \eta i \end{array} \quad \dots \quad (59)$$

where

$$\xi = -\frac{E}{4T} \text{ and } \eta = \sqrt{\frac{\rho E}{mT} - \frac{E^2}{16T^2}} \quad \dots \quad (60)$$

Hence from (39) we have

$${}_1a_0 = -{}_1b_0 = \frac{V}{c} \cdot \frac{1}{\lambda(a-\beta)} = \frac{V}{c\lambda} \cdot \frac{1}{2\eta}$$

Hence

$$\phi_1(ct) = \text{real part of } \frac{V}{2c\lambda\eta} \left\{ e^{(\xi+\eta)ct} - e^{(\xi-\eta)ct} \right\} \\ - \frac{V}{c\lambda\eta} \sin \eta ct,$$

and the pressure

$$F_1 = E\lambda \cdot \phi_1(ct) = \frac{EV}{c\eta} e^{\xi ct} \sin \eta ct \quad \dots \quad (61)$$

This naturally reminds one of Helmholtz's assumption that pressure may be taken as a harmonic function of time. Really it is a damped harmonic function of time.

If the impact happens to extend beyond the first epoch, the pressure co-efficients for the next epoch, *i.e.*, the second, can easily be calculated as follows:—

From (40), (41), (42), we have,

$${}_1a_0 = {}_1b_0 = \frac{V}{c} \cdot \frac{1}{\lambda^2(\alpha-\beta)^2} = \frac{V}{c\lambda^2} \cdot \frac{1}{(2\eta)^2} = \frac{V}{c\lambda^2} \cdot \frac{1}{8\eta^2} \quad \dots \quad (62)$$

$${}_1b_1 = \frac{V}{c} \cdot \frac{\xi+\eta}{\lambda^2(2\eta)^2} = -\frac{V}{c\lambda^2} \cdot \frac{\xi+\eta}{4\eta^2} \quad \dots \quad (63)$$

and

$${}_1a_1 = \frac{V}{c} \cdot \frac{\xi-\eta}{\lambda^2(2\eta)^2} = \frac{V}{c\lambda^2} \cdot \frac{\xi-\eta}{4\eta^2} \quad \dots \quad (64)$$

Hence the function  $\phi_2$  is given by

$$\phi_2(ct) = -\frac{V}{c} \cdot \frac{e^{\xi(ct-2a)}}{2\lambda^2\eta^2} \left[ \left\{ \frac{1}{2\eta\lambda} - \eta(ct-a) \right\} \sin \eta(ct-2a) \right. \\ \left. + \xi(ct-2a) \cos \eta(ct-2a) \right] \quad \dots \quad (65)$$

The pressure  $F_2$  is given by

$$F_2 = E\lambda[\phi_1(ct) + \phi_2(ct)] \quad \dots \quad (66)$$

The duration of impact is a root of the equation  $F_2(ct)=0$ , which however cannot be solved algebraically. In any case

a graphical solution is easily obtained. The pressure-functions for the third and succeeding epochs may be derived in the same manner.

#### § 4. REFLECTION FROM BOTH ENDS.

It has been assumed in the preceding articles that the end B of the string is so far away from the hammer at 0 that the impact ceases before any reflection from this extremity reaches the hammer. Our analysis can easily be extended to the case where B is not very far off. However the pressure function for the general case is too cumbrous for numerical calculation, hence we confine ourselves to the case, where the impact terminates after only one reflection has reached the hammer from the remote end. The method however is perfectly applicable to more complicated cases. Here it is necessary to make slight changes of notation.

Let

$f_1(ct \pm x - z)$  stand for

$$\frac{V}{c} \left[ e^{a(ct \pm x - z)} - e^{\beta(ct \pm x - z)} \right],$$

$f_2(ct \pm x - z)$  for

$$\frac{V}{c} \left[ e^{a(ct \pm x - z)} \left\{ 1 + a(ct \pm x - z) \right\} - e^{\beta(ct \pm x - z)} \left\{ 1 + \beta(ct \pm x - z) \right\} \right],$$

$f_3(ct \pm x - z)$  for

$$\frac{V}{c} \left[ e^{a(ct \pm x - z)} \left\{ 1 + 2a(ct \pm x - z) - \frac{a^2}{2} (ct \pm x - z)^2 \right\} \dots\dots\dots \right]$$

and so on.

Then the results of the previous articles may be reviewed in the following way:—

The wave  $f_1(ct - x)$  is reflected from the end A in the form  $-f_1(ct + x - 2a)$ . As soon as this reaches the hammer,



a new wave  $f_2(ct \pm x - 2a)$  is excited. The wave  $f_2(ct - x - 2a)$  is again reflected from A in the form  $f_2(ct + x - 4a)$ , which on reaching the hammer gives rise to another wave of the form  $f_2(ct \pm x - 4a)$ . Thus, if the end B is very remote, the displacements  $y_1, y_2$  are at any instant  $t$ , specified by  $(n-1)2a < ct < n.2a$ , expressed by

$$\sum_{r=1}^{s+1} f_r \{ ct \pm x - (r-1)2a \} - \sum_{r=1}^{s-1} f_r (ct + x - r.2a) \dots$$

It is obvious that the first term in the above represents the waves originating from the hammer and travelling in both directions, whereas the second term represents only reflections from the extremity A.

The first wave that reaches B has the form  $f_1(ct+x)$ . This is reflected in the form  $-f_1(ct-x-2b)$ , which on reaching the hammer gives rise to a new wave  $f_2(ct \pm x - 2b)$ . Of these, the wave  $f_2(ct+x-2b)$  travels towards B and we assume that the impact terminates, before its reflection, viz.,  $-f_2(ct-x-4b)$  reaches the hammer. Thus in all, two waves reach A at the same time, viz.,  $-f_1(ct-x-2b)$  and  $f_2(ct-x-2b)$ . Now let  $2b = s.2a + 2l$  where  $l < a$ . Then at an instant  $t$  specified by  $2b < ct < (s+1).2a$ , the displacements are

$$y_2 = f_2(ct-x-2b) - f_1(ct-x-2b)$$

$$+ \sum_{r=1}^{s+1} f_r \{ ct-x-(r-1)2a \} - \sum_{r=1}^{s-1} f_r (ct+x-r.2a)$$

and

$$y_1 = f_2(ct+x-2b) - f_1(ct+x-2b)$$

$$+ \sum_{r=1}^{s+1} f_r \{ ct+x-(r-1)2a \} - \sum_{r=1}^{s-1} f_r (ct+x-r.2a)$$

It is easily seen that at an instant  $t$  specified by  $(s+1)2a < ct < 2b+2a$ , the displacements are obtained simply by writing  $s+1$  for  $s$  in the upper limit of the summation occurring in the two foregoing expressions.

At the instant  $ct=2b+a$ , the displacements  $f_2(ct-x-2b)$  and  $-f_1(ct-x-2b)$  will undergo reflection at the end A which will reach the hammer at the instant  $ct=2b+2a$  in the forms  $-f_2(ct+x-2b-2a)$  and  $f_1(ct+x-2b-2a)$ , which will start fresh waves of the form  $f_3(ct\pm x-2b-2a)$  and  $-f_3(ct\pm x+2b-2a)$ . Thus at an instant  $t$  specified by  $2b+2a < ct < (s+2).2a$ , the displacements, if we write  $ct' = ct - 2b$ , are given by

$$\begin{aligned} y_s = & -f_2(ct'-x-2a) + f_3(ct'-x-2a) \\ & + f_1(ct'+x-2a) - f_3(ct'+x-2a) \\ & - f_1(ct'-x) + f_3(ct'-x). \\ & + \sum_{r=1}^{r=s+1} f_r \{ ct'-x-(r-1)2a \} - \sum_{r=1}^{r=s} f_r (ct'+x-r.2a). \end{aligned}$$

and

$$\begin{aligned} y_i = & -f_2(ct'+x-2a) + f_3(ct'+x-2a) \\ & + f_1(ct'+x-2a) - f_3(ct'+x-2a) \\ & - f_1(ct'-x) + f_3(ct'+x). \\ & + \sum_{r=1}^{r=s+1} f_r \{ ct'+x-(r-1)2a \} - \sum_{r=1}^{r=s} f_r (ct'+x-r.2a). \end{aligned}$$

This is easily generalised for an instant  $t$  specified by  $2b+s'.2a < ct < (s+1)2a+s'.2a$ , when the displacement  $y_s$  is given by

$$\begin{aligned} & - \sum_{r=2}^{r=s'+1} f_r \{ ct'-x-(r-1).2a \} + \sum_{r=1}^{r=s'} f_r (ct'+x-r.2a) \\ & + \sum_{r=2}^{r=s'+2} f_r \{ ct'-x-(r-2).2a \} - \sum_{r=2}^{r=s'+1} f_r \{ ct'+x-(r-1)2a \} \\ & + \sum_{r=1}^{r=s+s'+1} f_r \{ ct'-x-(r-1)2a \} - \sum_{r=1}^{r=s+s'} f_r (ct'+x-r.2a) - f_1(ct'-x). \end{aligned}$$

The displacement  $y_i$  is obtained by simply writing  $+x$  for  $-x$  in the left-hand side summations and leaving the rest

as it is. The pressure  $P$  of the hammer equals  $Eu$ , where  $u$  is the compression, and we get

$$\begin{aligned} P = Eu &= T \left( \frac{\partial y_s}{\partial x} - \frac{\partial y_r}{\partial x} \right)_{x=0} \\ &= 2T \left[ - \sum_{r=2}^{r=s'+1} f_{r'} \left\{ ct' - (r-1)2a \right\} \right. \\ &\quad + \sum_{r=2}^{r=s'+2} f_{r'} \left\{ ct' - (r-2)2a \right\} \\ &\quad \left. + \sum_{r=1}^{r=s+s'+1} f_{r'} \left\{ ct' - (r-1)2a \right\} \right] \end{aligned}$$

Let us denote by  $P_B$  the part of the pressure represented by the first two summations, i.e., those involving  $t'$ , so that

$$\begin{aligned} P_B &= 2T \left[ - \sum_{r=2}^{r=s'+1} f_{r'} \left\{ ct' - (r-1)2a \right\} \right. \\ &\quad \left. + \sum_{r=2}^{r=s'+2} f_{r'} \left\{ ct' - (r-2)2a \right\} \right]. \end{aligned}$$

It is easily seen that the values of  $P_B$  at the instants  $ct'=0, 2a, 4a$ , and  $6a$  are respectively the following:—

At	$ct'=0,$	$P_B = -2T\{-f_s'(0)\}.$
At	$ct'=2a,$	$P_B = -2T[f_s'(0) - \{f_s'(2a) + f_s'(0)\}]$
At	$ct'=4a,$	$P_B = -2T[f_s'(2a) + f_s'(0)$ $- \{f_s'(4a) + f_s'(2a) + f_s'(0)\}]$
At	$ct'=6a,$	$P_B = -2T[f_s'(4a) + f_s'(2a) + f_s'(0)$ $- \{f_s'(6a) + f_s'(4a) + f_s'(2a) + f_s'(0)\}].$

But since  $f_s'(0) = f_s'(0) = f_s'(0) = \dots = f_n'(0)$ , we see that at the instants given by  $ct'=2a, 4a$ , etc. no discontinuous rise of pressure takes place [see § 6]. The only discontinuity is at  $ct'=0$ , or  $ct=2b$ . In other words the secondary reflections from the end A originating from the first reflection

from B do not cause any discontinuous change of pressure. It is only at the instants  $ct=2b, 4b$ , etc., that reflections from B contribute a discontinuity. Hence, if we content ourselves with an approximation, wherein only the discontinuities arising from the reflections at B are taken into account, a general solution of the wave-problem where the reflections from both ends affect the hammer, may be obtained. If we denote by  $P_A$  and  $P_B$  the partial pressures due to successive reflections from the ends A and B respectively,

$$P_A = 2T \sum_{r=1}^{s'+1} f_r' \left\{ ct - (r-1)2a \right\}$$

and

$$P_B = 2T \sum_{r=2}^{s+1} f_r' \left\{ ct - (r-1)2b \right\}.$$

The resultant pressure at any instant is  $P_A + P_B$ , the summation extending over such values of  $s$  and  $s'$ , as satisfy at a given instant  $t$ , the following inequalities :—

$$\begin{aligned} & s'.2a < ct < (s' + 1) 2a \} \\ \text{and } & s.2b < ct < (s + 1) 2b \} \end{aligned}$$

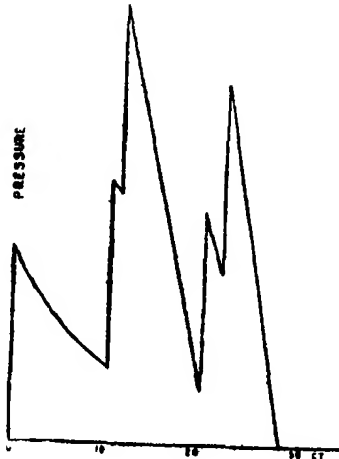


FIG. 2.

$$a = -0.1, \quad \beta = -\infty, \quad \alpha = 5 \text{ cms.} \quad b = 5.5 \text{ cms.}$$

## § 5. DURATION OF IMPACT.

The very complicated forms of the pressure function make it obvious that the duration of impact can be algebraically solved for in very rare cases. It is evident from (53) that the impact cannot terminate within the first epoch, unless  $\alpha$ ,  $\beta$  are imaginary. That leads us to the case of the soft hammer of § 3. The pressure is there given by (61),

$$\text{Pressure} = \frac{E \nu}{c \eta} e^{i c t} \sin \eta c t.$$

Now this can vanish for the value  $\mu\pi/c\eta$ , of  $t$ ; but if the impact terminates before the second epoch sets in, this value of  $t$  should not be greater than  $2a/c$ . That is,

$$\frac{\pi}{\eta} \leq 2a$$

If  $a$  is small,  $\eta$  has to be very large, but that is forbidden, because in a soft hammer,  $\eta$  must be small. Hence in order that the impact may terminate before any reflection reaches the hammer the length  $a$  should be rather large and the hammer very light and soft. Another tractable case is that of the rigid hammer. But even there, the solution is possible if the impact terminates within the first four epochs. For simplicity we confine ourselves to the second epoch only, the termination of impact within the first epoch being impossible. If we put  $F_2$  as given by (57) equal to zero, we get,

$$1 + e^{-2\alpha a} \left\{ 1 + \alpha (ct - 2a) \right\} = 0$$

$$\text{or } t = \frac{2a}{c} - \frac{1 + e^{2\alpha a}}{\alpha c} = \text{Duration of impact.}$$

The condition that the impact may not extend into the next epoch is that the above should not be greater than  $2a/c$ . Hence the limiting value of  $\alpha$  is given by

$$\alpha = -\frac{1}{2a} = \frac{m}{4\rho}$$

In other words, the length  $a$  should be greater than one-fourth the ratio of the mass of the hammer to the line density of the string.

To investigate whether there is any maximum or minimum in the curve of  $t$  against  $a$  we put  $\frac{dt}{da} = 0$ , and get  $e^{2aa} = \frac{1}{a}$  which leads to imaginary values of  $a$ . Hence provided that the impact is confined to the second epoch, the duration of impact does not pass through any maximum or minimum, but increases with the length  $a$ .

Similarly, if the impact ceases in the third or the fourth epoch, the equation for the duration of impact is of the third or the fourth degree respectively, and can be algebraically solved. But they lack elegance and simplicity. However the method of graphs is applicable in all cases.

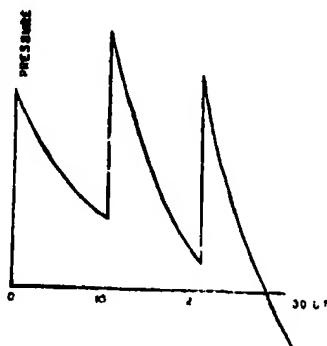


FIG. 3.

$$\begin{aligned} a &= 5 \text{ cms.} & b &= \infty \\ a &= -0.1, & \beta &= -\infty \end{aligned}$$

#### § 6. GENERAL.

A glance at the formulae will show that the pressure at any instant is directly proportional to the initial velocity  $V$  of the hammer. Further interpretation of these formulae is best done by means of a series of graphs. To simplify curveplotting

we have assumed the quantities  $\rho$ ,  $v$ ,  $c$  to have the same values in all cases and the graphs are all drawn on the same scale. We shall first illustrate the gradual change in the form of the pressure as we pass from the rigid to the elastic hammer. In figures No. 3, 4, and 5 we have taken  $a$  or  $-2\rho/m$  to be  $-1/10$ , which probably represents very nearly the actual state of affairs in a modern pianoforte. Of the three figures just referred to, the first corresponds to a perfectly rigid hammer for which  $\beta$  or  $-E/2T$  is infinitely large, the second and the third having  $\beta = -10$  and  $-1$  respectively.

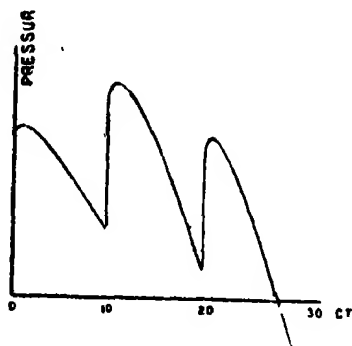


FIG. 4.

$$\begin{aligned} a &= 5 \text{ cms.}, & b &= \infty, \\ a &= -0.1, & \beta &= -10 \end{aligned}$$

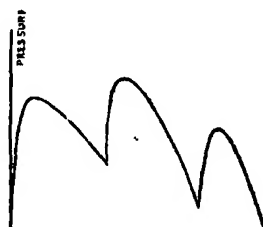


FIG. 5.

$$\begin{aligned} a &= 5 \text{ cms.} & b &= \infty \\ a &= -0.1, & \beta &= -1 \end{aligned}$$

In all these cases the distance of the near end A of the string from the point of impact is 5 cm. The figures show that the impact ceases in each case in the third epoch. It will be observed that at the beginning of each epoch there is a sharp, discontinuous increase of pressure of the rigid hammer. The hammer which comes next in the order of hardness has not got any such discontinuity in the value of pressure, but the direction of the curve at these points changes discontinuously and a sharp rise of pressure immediately after an epoch has set in is still to be noted.

Figure 5 which represents the softest of the three, points to a still slower rise of pressure at these instants and the sharp angularities of the previous figures give place to a more rounded form. Figure 6 represents the case of the really soft hammer of § 3, *i.e.*, one for which  $E$  is small compared with  $T$ . Here we take  $E/T=1/25$  and  $\rho/m=1/16$ , so that  $\xi=-0.02$ ,  $\eta=0.05$  and  $1/\lambda=0.04$ . We have shown in § 3 that if the impact is to extend well into the second epoch, then  $\pi/\eta > 2a$ , *i.e.*,  $2a$  should be less than 63 cm. We have taken  $2a=50$  cm. In Figure No. 7, we still take  $2a=50$  cm,  $\rho/m=1/16$ , but  $E=\infty$ . This figure has been added to show the sharp contrast between the perfectly rigid and the very soft hammer. Fig. 2 represents the case where reflections from both ends affect the motion of the hammer, as discussed in § 4. Here we take  $a=-.01$ ,  $2a=10$ ,  $2b=11$ . A comparison of Figures Nos. 2 and 3 will show that the impact ceases in both in the third epoch, but the values of the pressure maxima in the first case are much larger than in Figures Nos. 3, 4 and 5. Since the area bounded by the curve and the  $t$  axis is proportional to the total change of momentum of the hammer, this hammer rebounds with greater violence from the string represented in Figure No. 2 (*i.e.*, a short string), than from one in Figures Nos. 3, 4 and 5 (*i.e.*, a long string), other conditions remaining the same.



FIG. 6.

$$a=25 \text{ cms. } b=\infty, \quad \xi=-0.02, \quad \eta=0.05$$



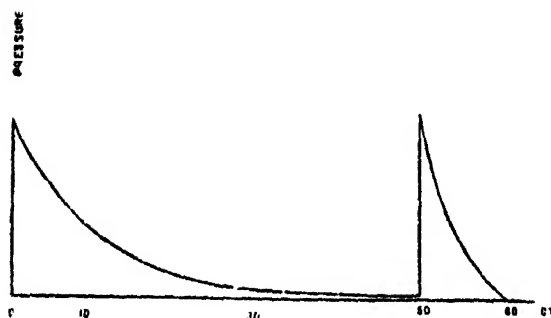


FIG. 7.

$$\alpha = 25 \text{ cms.} \quad b = \infty, \quad a = -0.125, \\ \beta = -\infty$$

A study of the Figures Nos. 3, 4 and 5 will show that when the hammer is very nearly rigid, a slight diminution in the hardness of the hammer does not alter very much the duration of the impact, although there is a sensible lengthening out of the same, if we abruptly pass from a rigid to a very soft hammer, as Figures Nos. 6 and 7 will show. Since the relative intensities of the higher harmonics increase with the rise in the values of the pressure-maxima of these curves, these higher harmonics must grow feebler as we pass on from a rigid to an elastic hammer, the latter having another advantage over the former in this respect, in that the impact also lasts longer there.

A further extension of the theory which takes into account the variation of the area of contact between hammer and the string on the basis of Hertz's theory of impact is being undertaken.

My best thanks are due to Professor C. V. Raman for his valuable advice in my preparation of the paper.

## 8

# The Scattering of Light by Sputtered Metallic Surfaces.

BY

L. A. RAMDAS, M.A.,

PALIT RESEARCH SCHOLAR, UNIVERSITY OF CALCUTTA.

### CONTENTS :

- (1) Introduction and Summary.
- (2) Description of sputtering apparatus.
- (3) Optical study of the sputtered films.

#### (1) *Introduction and Summary.*

The scattering of light by the free surfaces of transparent liquids and liquid mercury has been recently dealt with in a series of papers.<sup>1</sup> The author had, in an earlier paper<sup>2</sup> described the scattering of light by clean solid surfaces. It has been shown that in the case of liquids the effect is due to roughness arising from thermal agitation at the surface. In the case of the cleavage surface of a crystal, such as mica, this roughness is absent as the atoms are arranged in a regular space lattice and so there is no scattering of light to be observed. In the case of ordinary metallic surfaces obtained by polishing, we get a relatively intense scattering of light, the origin of which is not far to seek, as such surfaces exhibit numerous imperfections when seen under a microscope

<sup>1</sup> O V Raman and L. A. Ramdas, Proc Roy Soc A. Series, 1925, Vol 108, pp 561-71 ; Vol 109, pp. 150-7 ; Vol. 109, pp 272-80.

<sup>2</sup> L. A. Ramdas, Proceedings of the Indian Association for the Cultivation of Science, Vol. IX, Part II, pp 129-143.

in strong illumination. Finely polished mirrors of steel and speculum and metallic mirrors obtained by cathode sputtering on glass and subsequently polished on the front scatter much less light but even here a microscopic examination shows that the surfaces are far from possessing the degree of optical perfection set by a really clean surface of liquid mercury. Experiments were made by the author on metallic films of gold and silver obtained by cathode sputtering on freshly cleaved surfaces of transparent mica and it was found that the *mica metal* contact surfaces illuminated and observed through the mica showed an extremely feeble and bluish opalescence indicating a surface nearly but not ideally perfect like a fresh mica surface. The intensity of this scattering in the case of gold was found to be much feebler than the scattering by a clean mercury surface. The results obtained with these surfaces are described in the following sections.

## (2) *Description of Sputtering Apparatus.*

This consisted of a glass bell-jar resting on a deep circular groove cut in a thick circular iron plate. The mouth of the bell-jar was closed by a rubber stopper through which a long iron wire nearly reaching the bottom and an exit tube passed. After screwing on a small disc of the metal whose deposit is required and placing a clean sheet of mica on a cup just below the metal disc, the bell-jar was fitted into the groove permanently by means of sealing wax. This was done by previously heating the iron plate and filling the groove with molten sealing wax. After placing the bell-jar on the groove and allowing to cool, the wax-joint became quite vacuum-tight. The rubber stopper joint above was also covered with sealing wax. The evacuation of the sputtering chamber was performed by means of a Gaede Mercury pump backed by a box pump, and, when the vacuum was sufficiently high, an induction coil discharge was passed

through. The iron plate was the anode and the metallic disc the cathode.

It was found by trial that if the current exceeded three to four milli-amperes the deposit consisted of small crystals throughout the thickness of the film. These crystals were quite visible to the naked eye. For low currents, however, only the free surface was covered with crystals which could be detected with a microscope while the *mica-metal* contact surface was found to be absolutely structureless even with a high power microscope. For gold, a current of three to four milli-amperes running for ten hours gave a thick opaque deposit. After the sputtering was over dust-free air was slowly let into the bell-jar and, after softening the sealing wax at the joint below by sufficient heating, the bell-jar was removed and the mica sheet quickly transferred into a suitable tube blackened inside and provided with two glass windows at the open ends. The windows were fixed with wax. These precautions are essential to keep the surfaces dust-free. In the case of all metals except gold which have been tried, the films rapidly deteriorate by slow oxidation. Arrangements are being made to preserve them in vacuum as soon as the deposition is over.

### (3) *Optical Study of the Sputtered Films.*

A horizontal beam of sunlight was reflected into the dark room through a small aperture by means of a heliostat. This beam was passed through a lens and the surfaces to be examined placed at the focus. It is evident that glass surfaces cannot be used for obtaining the sputtered films as even a freshly cracked surface of glass scatters enough light to mask the feeble effects we are looking for. Mica is very suitable as freshly cleaved surfaces do not scatter any light. If the *free* surface of the deposit on mica was placed at the focus, it was found to scatter very much less than the

*polished* surfaces which had been examined before. When the focal spot was examined with a microscope the surface was found to consist of small, uniformly distributed micro-crystals which appear like fine specks. The size of these crystals depends on the current density and in some cases on the same deposit it varied continuously from the centre giving rise to a series of coloured rings arising from diffraction of light by these crystals. These effects require more detailed study and we proceed to the examination of the *mica-metal* contact surface which is really more interesting.

On placing this surface at the focus careful examination reveals an extraordinarily feeble and bluish opalescent spot. The intensity of the spot was smaller than in the case of liquid mercury but the distribution of the intensity in different directions was very much like that in the case of the mercury surface, *i.e.*, fairly uniform when the incident light is unpolarised. Detailed observations of the polarisation effects require some care as one has to observe through mica, but they can be made by previously marking the suitable directions in which the primitive polarisation would be unaltered by transmission on the mica piece before depositing the metal and mounting it.

The intensity of scattering of the gold-mica surface was compared photographically with the scattering by mercury and it was found to be less than one-fifth of the latter. While a mercury surface scatters about a ten-millionth part of the incident beam per unit solid angle, the gold-mica surface scatters only about a fifty-millionth part ( $2 \times 10^{-8}$ ) of the incident beam. This is the smallest ratio till now obtained for scattering by a metallic surface.

The remarkably high optical perfection of the mica-gold boundary indicates that the part of the film in actual contact with the mica surface does not consist of discrete crystalline aggregates of microscopic size but is a more or less perfectly uniform structure of either individual atoms or of aggregates

containing only a small number of atoms which have cohered into a uniform structure. The structure of sputtered films of gold and silver has been studied by H. Kahler<sup>1</sup> by using mono-chromatic X radiation and the diffraction patterns show that the film is composed of very small crystalline aggregates. It may be pointed out that the non-crystalline nature of the *mica-metal* contact surface will be masked by the crystals which later form or adhere upon it as the deposition goes on and that we have no means of detecting its presence except by the optical method above described.

More detailed work with sputtered films of other metals is being undertaken. The present investigation was taken up at the suggestion of Prof. C. V. Raman, F.R.S. and carried out in his laboratory at Calcutta.

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<sup>1</sup> Physical Review, Vol. XVIII Series 2, 1921, p 210.

## Behaviour of Silicic Acid Gel during the Drying-up Process.

BY

K. KRISHNAMURTI, M.Sc.

Nearly two years ago in the course of my work on hydrated silica, I observed the following interesting phenomenon :—

Silicic acid gel, prepared by the hydrolysis of silicon tetrachloride, was well washed and treated with a saturated solution of potassium chloride. The whole was transferred to a Gooch crucible and the excess of solution removed by suction. The gel was left exposed to the air inside the drawer. These experiments were conducted during the summer months (April and May) of 1924. The silicic acid continually lost water in the dry air, thus experiencing a large contraction, during which a considerable amount of pressure is exerted upon the capillaries of the gel. This is manifested by the growth (shown in the fig) which consists of thin, white glistening fibres of potassium chloride. It was noticed that the growth was not

so marked during the first few days, and became quite prominent in about a month. Evidently the pressure exerted during the later stages when the amount of water present is small, is much greater than that at the beginning of the drying-up process.

This seems to be an interesting modification of potassium chloride, the exact nature of which can be elucidated by X-ray analysis. A similar growth has also been obtained when silica powder is treated with potassium chloride solution and then allowed to dry up, though, in this case, the fibres are much shorter and thinner. The author hopes to investigate if other gels behave in a similar manner.

Long after this note was written, I happened to notice a similar observation made by Messrs. H. A. Fells and J. B. Firth in the *Journal of Physical Chemistry* of March, 1925 (p 245) which reached us on the 14th Feb. 1926. The above paper appears to have been communicated by the authors on October 18, 1924, whereas my observations were made much earlier (in May, 1924).

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# On the Total Reflexion of Light.

BY

PROF. C. V. RAMAN, F.R.S.

(Continued from page 286)

## 5. *Effect of Diffraction on the Sharpness of the Boundary of Total Reflection.*

The intensity of the light reflected at the boundary between two media is unity when the incidence is at or more than at the critical angle. For incidences at less than the critical angle, the intensity of reflexion falls off considerably. The curve which exhibits the variation of the intensity of internal reflexion with the angle of incidence exhibits a sharp right-angle bend at the critical incidence. It is easily verified from the Fresnel formulae that the differential co-efficient of the function expressing the relationship is discontinuous at this point, changing suddenly from infinity to zero. In this sense, the boundary of total reflexion as given by the Fresnel formulae is infinitely sharp, and indeed in practice, it is the very rapid falling-off in the intensity of reflection at less the critical incidence that enables the boundary of total reflection to be visually observed. .

The Fresnel theory is, of course, based on the assumption of an infinite area of surface being operative. We have already seen that our diffraction-integrals for the second medium when taken over an infinite area exhibit a discontinuity when  $\mu \sin \phi = 1$ , and that in this region a stricter treatment would require the finite area of the surface being taken into account. When the aperture is limited, the energy diffracted into the second medium from the margins of the surface is not a negligible proportion of the whole and must be

deducted from that incident to obtain the energy of the reflected pencil. In other words, with finite apertures, the sharpness of the boundary of total reflection must disappear, and we should obtain a smooth curve connecting the intensity of reflection and the angle of incidence and not a curve showing a sharp bend.

Theory thus indicates that with surfaces of finite area, the boundary of total reflection must be distinctly less well defined than with extended surfaces. To test this idea, some observations were made by the writer with a totally reflecting prism of glass. The hypotenuse of the prism was first covered over with black paint, and then a strip of the paint, parallel to the edges of the prism was removed from the middle of the face. A white sheet of cardboard illuminated by the green light of a mercury arc was viewed by internal reflection from the open strip of surface of the prism. The boundary of total reflection could be seen as a fairly sharp curve when the width of the strip of surface was 2 mm. or more; but when it was less than 2 mm., there was a distinct deterioration, and with  $\frac{1}{2}$  mm. wide strip of surface, the lack of sharpness of the boundary of total reflection became quite conspicuous.

Drude gives the following figures for the relation of the intensity of the reflected light as a fraction  $I$  of the incident energy and the angle  $\gamma$  by which the incidence falls short of the critical angle for a glass surface of refractive index 1.51.

$\gamma$	0'	2'	4'	8'	15'
$I$	1.0	0.74	0.64	0.53	0.48

An aperture  $\frac{1}{2}$  mm. wide held at  $45^\circ$  would give a diffraction-pattern of which the central band would be fully 10' wide, ( $\lambda = 5000 \text{ \AA-U}$ ). The observed disappearance of the sharpness of the boundary of total reflection by a surface of the width stated is quite intelligible in the light of these figures.

### 6. *Some Critical Remarks on Schuster's Recent Paper.*

In view of the preceding discussion, it is not perhaps necessary to comment at any length on Prof. Schuster's recent paper already referred to in the introduction. Schuster has suggested that the assumption of an indefinitely extended boundary in the usual treatment is essentially illegitimate. With regard to this question, it should, I think, be emphasised that the changes of phase which occur in total reflexion are intimately related to the disturbance penetrating into the second medium, and the fact that the theory is in agreement with experiment in this respect, must be regarded as indicating that the disturbance at points close to the boundary is correctly given by the theory in which the aperture is regarded as infinite. In other words, diffraction at the edges of the illuminated area of the boundary, even if it does give rise to observable effects elsewhere, does not sensibly modify the character of the superficial disturbance at points close to boundary. Further, it has to be pointed out that the diffraction effects contemplated in Schuster's theory do not agree with those actually observed and described in my paper in the *Phil. Mag.* for October, 1925; this disagreement with facts arises from the circumstance that the treatment given is somewhat artificial and does not follow the essential physical features of the case. Schuster's treatment is based on an extension of the analogy which exists between the problem of diffraction by an obliquely-held aperture and that of nearly grazing emergence from the plane boundary between two media. This analogy has been extensively studied by the present writer and his pupils in earlier papers. It is found that the diffraction-patterns observed in the three cases, *viz.*, oblique reflexion from a plane mirror, oblique transmission through an aperture bounded by parallel edges, and oblique emergence from a surface on which light is incident at nearly the critical angle,

show very similar features; and the analogy is certainly useful up to a certain point. But when we proceed beyond the natural limits of the analogy and compare the case in which light is incident on a glass surface at more than the critical angle with the cases in which a reflecting mirror is held so that no light falls upon it, or an aperture is so held that no light passes through it, it is found experimentally that the parallelism previously noted ceases to exist. This is not surprising, in view of the essential difference subsisting between the cases. In the case of total reflection, the boundary between the two media is *fully illuminated*, and each element of its area considered as a unit is free to emit secondary wavelets into the second medium. Indeed, in consequence, a notable amount of diffracted light does emerge into the second medium. In the two other cases, on the other hand, when a reflecting surface or a transmitting aperture is tilted from the normal position through more than  $90^\circ$ , the surface or aperture ceases to receive the illumination of the primary waves, and its elements can no longer emit secondary waves as previously; the diffraction pattern becomes very feeble or practically disappears in consequence. Prof. Schuster's treatment of total reflexion overlooks this fundamental difference, and it is not surprising therefore that the phenomena observed do not fit in with his theory.

### 7. Summary.

The paper considers the phenomena of total reflection from the point of view of diffraction-theory.

(a) The effect at any point in the second medium not far from the surface is given by the integral

$$\text{Const.} \int_0^\infty \int^{2\pi} \frac{A}{\lambda(s^2 + r^2)^{\frac{1}{2}}} \cos. \frac{2\pi}{\lambda} \{Vt - (s^2 + r^2)^{\frac{1}{2}} \\ - r. \mu \sin \phi \cos. \theta + \epsilon\} r dr d\theta$$

This is evaluated by the aid of certain definite integrals given by Sonine and by Lamb, and it is shown that when  $\mu \sin \phi < 1$  it reduces to

$$A \cos. \frac{2\pi}{\lambda} (Vt - x\mu \sin \phi - z\sqrt{1 - \mu^2 \sin^2 \phi})$$

which is the ordinary expression for the refracted wave.

(b) When  $\mu \sin \phi > 1$  (the case of total reflection), the integral reduces to

$$A \cos. \frac{2\pi}{\lambda} (Vt - x\mu \sin \phi). e^{-\pi \frac{2\pi}{\lambda} (\mu^2 \sin^2 \phi - 1)^{\frac{1}{2}}}$$

which is of the same form as the well-known law of the superficial undulation close to the surface derived from Fresnel's investigation of total reflection. The superficial undulation is shown to be a diffraction-effect arising from the immediate vicinity of the point of observation.

(c) When the integration is made over a finite area of the surface, we get additional effects which arise from the margins of the diffracting area and can be perceived as diffracted streams of light reaching points considerably removed from the surface.

(d) The boundary of total reflection by an extended surface is infinitely sharp in the sense that the curve connecting the intensity of reflection and the angle of incidence shows a sharp bend, the tangent of the angle of slope changing discontinuously from infinity to zero.

(e) When, however, we consider a surface of finite area, the boundary of total reflection is no longer infinitely sharp, but is rounded off to an extent depending on the width of the aperture. This has been verified experimentally.

(f) Some critical remarks are offered on a recent paper of Schuster on total reflection.

## ANNUAL REPORT FOR THE YEAR 1923.

1. The Committee of Management beg to submit the following report showing the work done by the Association during the year under review.

2. The Physical Laboratory of the Association continued as usual to be a centre of active research in various branches of the science, and attracted workers from different parts of India and Burma. The following list of papers which were contributed from the Laboratory of the Association or published in its Proceedings during the year 1923 may serve as an indication of the volume of the research work in which the Association has co-operated.

### PROCEEDINGS OF THE INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.

#### *Vol. VIII, Parts I and II.*

1. Electromagnetic Theory of the Scattering of Light in Fluids—by K. R. Ramanathan, M.A.

2. The Scattering of Light by Liquid Droplets, and the Theory of Coronas, Glories and Iridescent Clouds.—by Bidhu Bhushan Ray, D.Sc.

3. Earthquake Coda—by S. K. Banerji, D.Sc.

4. The Chronographic Determination of Acceleration of Gravity—by Durgadas Banerji, M.Sc.

5. The Oscillations of Spheroidal Drops and the Phenomena of the Spheroidal State—by Rajendra Nath Ghosh, M.Sc.

6. Mersenne and his Ideas on Sound—by J. W. Giltay.
7. Investigations on the Acoustics of the Pianoforte I,—by Susil Krishna Datta, M.Sc.
8. The Temperature Variation of the Electrical Conductivity of Copper and Iron Fused with Mica.—by K. R. Ramanathan, M.A., D.Sc.
9. Effect of Barriers on Ripple-Mark—by S. K. Banerjee, D.Sc.
10. The Diffraction of X-rays in Liquids, Liquid Mixtures, Solutions, Fluid Crystals, and Amorphous Solids—by C. V. Raman, M.A., D.Sc., and K. R. Ramanathan, M.A., D.Sc.

#### PROCEEDINGS OF THE ROYAL SOCIETY.

1. The Molecular Scattering of Light in Carbon Dioxide at High Pressures—by Prof. C. V. Raman and Dr. K. R. Ramanathan.

#### PHILOSOPHICAL MAGAZINE.

1. On the Molecular Scattering of Light in Dense Vapours and Gases—by Prof. C. V. Raman and Dr. K. R. Ramanathan.
2. On the Molecular Scattering of Light in Liquid Mixtures—by Prof. C. V. Raman and Dr. K. R. Ramanathan.
3. On the Molecular Scattering and Extinction of Light in Liquids and the Determination of the Avogadro Constant—by Prof. C. V. Raman and K. Seshagiri Rao.
4. On the Polarisation of the Light Scattered by Gases and Vapours—by Prof. C. V. Raman and K. Seshagiri Rao.
5. On the Colour of the Sea—by Dr. K. R. Ramanathan.

## ASTROPHYSICAL JOURNAL.

1. On the Visual and the Photographic Albedo of the Earth—by Mr. K. R. Ramanathan.
2. On the Spectrum of Neutral Helium—by Prof. C. V. Raman and A. S. Ganesan.

## NATURE.

1. Thermal Opalescence in Crystals and the Colour of Ice in Glaciers—by Prof. C. V. Raman.
2. The Scattering of X-rays in Liquids—by Prof. C. V. Raman.
3. The Nature of the Liquid State—by Prof. C. V. Raman.
4. A Theory of the Viscosity of Liquids—by Prof. C. V. Raman.
5. The Viscosity of Liquids—by Prof. C. V. Raman.
6. The Scattering of Light by Anisotropic Molecules—by Prof. C. V. Raman.
7. The Scattering of Light by Liquid and Solid Surfaces—by Prof. C. V. Raman.

## PHYSICAL REVIEW.

1. Molecular Scattering of Light in Benzene, Vapour and Liquid—by Mr. K. R. Ramanathan.
2. Fresnel's Laws of Reflection, Note on a departure from—Mr. Nalini Kanta Sur.
3. Molecular Scattering of Light in Liquid Mixtures—by Mr. J. C. Kameswar Rav.



## BULLETIN OF THE CALCUTTA MATHEMATICAL SOCIETY.

1. On the Spectra of Isotopes—by Mr. Panchanon Das.
2. Ripples of Finite Amplitude on a Viscous Liquid—by Mr. J. C. Kameswar Ray.
3. On the Secondary Spectrum of Hydrogen—by Mr. Panchanon Das.

Early in the year under report, your Honorary Secretary attended the Science Congress at Lucknow as Honorary General Secretary of that organisation and received the thanks of the Congress for the success of the arrangements for the meeting. The rest of the year, except for a few weeks' absence at Shillong during the Poojah holidays, was taken up with the regular work of lecturing and research. An item of scientific interest noted during the holiday at Shillong was the remarkable clear visibility of the Himalayan snows from Shillong, a distance of about 150 miles. Some quantitative studies of this phenomenon would be of interest.

Dr. K. R. Ramanathan of the Rangoon University was working in our laboratory on the molecular scattering of light in carbon dioxide at high pressures and on the electro-magnetic theory of light scattering in fluids.

Mr. K. Seshagiri Rao, research scholar of the Madras University, was continuing his work on the scattering of light in gases and the diffraction of light by mixed plates.

Mr. N. C. Krishnaiyer, Professor of Physics, University College, Rangoon, worked in this laboratory on the scattering and absorption of light in didymium glass.

Mr. J. C. Kameswar Ray was working on the scattering of light by liquid mixtures.

Mr. L. A. Ramdas was working here on the molecular scattering of light by liquid and solid surfaces and on the effect of temperature on the polarisation of the light scattered by carbon-dioxide.

Mr. Thaka Prasad Biswas was engaged in constructing an apparatus for measuring the viscosity of gases and vapours.

Mr. D. N. Bhattacharya, Professor of Physics, Behar National College, Bankipore was working on the scattering of light by carbon-dioxide at the critical temperature.

Mr. A. S. Ganesan, Research Scholar of the Madras University was working on the spectrum of neutral helium, on the scattering of light by liquids and gases at various angles and on chromatic emulsions.

Mr. Manindra Nath Mitra of the Presidency College, Calcutta, was working on the nature of the vibrations of the Trevelyan rocker.

Mr. Krishnapada Ghosh was trying to find out whether soap bubbles are doubly refracting.

Mr. K. S. Krishnan was working on the scattering of light by a large number of pure liquids.

Mr. N. Majumdar was working on the absorption of light by Carbon-di-sulphide.

Mr. Sunderlingam was engaged in preparing a large number of bulbs containing pure liquids for the study of scattering.

Babu Sukumar Ghosh was engaged in the study of viscosity of liquids and vapours and of broken bows.

Mr. R. Venkataswara Iyer of the Rangoon University was working on the scattering of light by pure liquids.

### *Applied Electricity Class.*

During the latter part of the year under report your Honorary Secretary undertook to deliver a course of lectures on Applied Electricity. Some 36 students took admission in the above class and about 20 lectures were delivered on the subject.

## DEPARTMENT OF CHEMISTRY.

Owing to financial stringency, the Commercial Analysis Class had to be closed in May, 1923, and the chemical laboratory thus came on the same footing as the physical laboratory as a purely research institution. The chemical laboratory rendered very useful assistance in the purification of chemicals, etc., for work on the physical side; research work in organic chemistry has also been taken up, further details regarding which will appear in the report for 1924.

## BOTANY DEPARTMENT.

The required number of lectures in Botany for I.A. and I.Sc. students were delivered by Profs. Jyotish Chandra Pal and Rajkumar Sen and the practical classes were held by these professors with the assistance of a demonstrator.

The test examination of the 2nd-year Botany Class was held in due time. The first three students will be awarded prizes. Their names are given in order of merit.

1. Jadab Lal Banerjee.
2. Manindra Nath Chakravarty.
3. Pravat Kumar Rai Choudhury.

## LIBRARY.

The following publications were subscribed for as usual :-

1. Scientific American Monthly.
2. Nature.
3. Science Abstracts, A & B.
4. American Journal of Science.
5. Philosophical Magazine.
6. Botanical Gazette.
7. Annals of Botany.

8. Astrophysical Journal.
9. Chemical News.
10. Proceedings of the Royal Society, A & B.
11. Transactions of the Royal Society, A. & B.
12. Annalen der Physik.
13. Physikalische Berichte.
14. Zeitschrift für Physik.
15. Physikalische Zeitschrift.
16. Encyklopadie der Mathematischen Wissenschaften.
17. Collegian.

The Committee of Management have to acknowledge with thanks the presentation of Journals and Periodicals in exchange from the following Societies and institutions :

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Faraday Society.
8. Franklin Institute.
9. American Geographical Society.
10. South African Association for the Advancement of Science.
11. Sitzungsberichte of the Prussian Academy of Sciences, Berlin.
12. Sitzungsberichte of the Academy of Sciences, Vienna, Austria.
13. University of Pennsylvania, Philadelphia.
14. Museum Journal of the University of Philadelphia.
15. Le Journal de Physique et le Radium of the Physical Society of France.
16. Publications of the Royal Canadian Institute.
17. Technological and Scientific papers and Circulars of the Bureau of Standards.

18. University of Iowa.
19. University of Calcutta.
20. Calcutta Mathematical Society.
21. Government of India.
22. Government of Bengal.
23. Government of Mysore.
24. University of Bombay.
25. Government of Bombay.
26. University of Allahabad.
27. University of Punjab.
28. Agricultural Research Institute, Pusa
29. Asiatic Society of Bengal.
30. Indian Institute of Science, Bangalore.

The Committee of Management express their grateful thanks to Rai Chunilal Bose Bahadur, C.I.E., I.S.O., M.B., F.C.S., etc, and to the Honorary Secretary for presenting the Journal of the Chemical Society, London, and the Journal of the Indian Mathematical Society respectively to the Association.

The thanks of the Association are due to the Editors of the *Englishman*, *Bengalee*, *Forward*, *Servant* and *Basumati* for gratuitously supplying to the library of the Association their widely circulated daily newspapers and publishing in their columns the daily Meteorological reports of this Institution.

Our senior mechanic Babu Bepin Chandra Mullik who was a very efficient man died during the year under report, and in his place a new mechanic Babu Dharendra Nath Das was appointed. He and his assistant made the following appliances:

1. Nozzle for lantern lens.
2. Plugs for X-ray coil.
3. Vanes with shaft to keep temperature constant in a bath,

4. Condenser for keeping cross pipe ends cool.
5. Cross tube, with sockets.
6. Six milling cutters.
7. Three mandrels for the same.
8. Dividing spring for small lathe.
9. Fitting a motor for lathe.
10. Fitting a pulley in small motor.
11. Fitting counter shaft for lathe.
12. Fitting up Regulator and switch board for a small motor.
13. Fitting up Brackets, etc., for counter shaft.
14. Making a Lead box for X-ray work.
15. Fitting up a Steel tube for observing scattering of light, under high pressure.

Besides these many other repair works and fittings for research work were executed.

### *Laboratory Equipment.*

The following apparatus and materials were purchased during the year 1923.

1. One Analytical Balance.
2. One X-ray Spectrometer.
3. (a) One Quartz fluorite Objective.  
(b) One Quartz Sphere.  
(c) One Analyser for ultra violet.  
(d) One 45° reflecting prism.  
(e) Two double image prisms (in optical contact).  
(f) Two fused Quartz discs.
4. One Cylinder of Argon with valve.
5. 75 lbs. mercury.

The mounting of the large concave grating was proceeded with and some progress was made.

A motor-pump for supplying water to the laboratory was purchased and installed. This has proved a great convenience.

*Financial Position.*

On the 31st December, 1923, the Association had in the custody of Imperial Bank of India, Government securities of the value of Rs. 2,32,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 2,707-0-4, and a cash balance in the office of Rs. 218-14-0, amounting in all to Rs. 2,41,825-14-1.

On the 31st December, 1922, the Association had in the custody of the Imperial Bank of India, Government securities of the value of Rs. 2,30,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 3,349-5-6, and a cash balance in the office of Rs. 241-4-6, amounting in all to Rs. 2,40,490-10-0.

The thanks of the Association are due to His late Highness the Maharaja of Cooch-Behar, G.C.I.E., etc., for his generous contribution of Rs. 100 per month which was continued up to March, 1923, and also to Babu Nirmal Chundra Chander, M.A., B.L., who very kindly continued his annual subscription.

A special donation of Rs. 1,000 was received from the Vizianagram Samsthanam for equipping the Laboratory, etc., for which the Committee of Management offers its grateful acknowledgment.

*Acknowledgment.*

The thanks of the members of the Association are due to their Honorary Engineers Rai Krishna Chandra Banerjee, and Babu Bhabadev Chatterjee, to their Honorary Legal Advisers

Babus Jatindra Chandra Bose and Nirmal Chandra Chander, to their Honorary Auditor, Babu Ishan Chandra Bose, to their Honorary Secretary, Prof. C.V. Raman, and to their Honorary Assistant Secretaries, Babus Jyotish Chandra Pal and Ashutosh Dey for their gratuitous services.

### *Obituary*

The loss by the death of our President Raja Peary Mohan Mukerjee which occurred during the year under report was a very grievous one. The proceedings of the special meeting held in connection with it have been recorded in the report for 1922.

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*Balance sheet as on the 31st December, 1923.*

To	Rs.	AS.	P.	By	Rs.	AS.	P.
Government Securities 3½% Fund	General	2,32,400	0	0	General fund	..	3,88,197 15 8
Government Securities 3½% Professorship fund	Ripon	6,000	0	0	Ripon Professorship fund	.	10,830 0 0
Government Securities 3½% Professorship fund	Ripon	6,000	0	0	H. H. the Maharaja of Cooch-Behar Professorship fund.	21,510	0 0
Government Securities Nikunja Garabhai fund	Nikunja Garabhai	500	0	0			
Value of land and old building		31,680	11	9	Hare Professorship fund	..	1,025 0 0
Lecture Hall & Gallery	...	23,465	5	3	Victoria Professorship fund	.	1,000 0 0
Vizianagram Laboratory		40,900	14	0	Dr. Sircar Memorial fund	...	10,584 8 3
Range of Shops (East Side)	.	2,516	10	9	Deposit accounts	...	451 14 0
Range of Shops (West Side)	...	2,308	5	0	Vizianagram fund account	..	1,340 0 0
Durwan's room	.	303	13	9	Provident fund account	...	3,120 9 10
Servants' quarters		1,024	0	0	Medal fund, Wood-burn	..	500 0 0
Observatory	.	3,320	9	9	Dr. Mahendralal Sircar	..	3,000 0 0
Bonus of Provident fund	...	1,922	0	0	Joykissen Mukerji	...	9,339 0 0
Contribution to Provident fund account		1,988	9	10	Nikunja Garabhai	...	500 0 0
Scientific Instrument account General.. fund		45,260	11	8	Jatindra Chandra	...	550 0 0

"	"	K. K. Tagore fund	25,000	0	0	Interest account Dr. M. L. Sircar Medal fund	525	0	0	
Botanical Instrument account	...		2,329	6	0	"	Ripon Professorship fund	5,906	10	3
Library account	...		24,933	0	7	"	Nikunja Garabini fund	196	2	2
Tools and Implements account	.		161	12	3	"	Wood-burn Medal fund	106	8	0
Workshop Instrument account	..		9,592	2	3	"	Jatindra Ch. Prize fund	96	11	0
Sir Richard Temple Prize account	..		245	0	0					
Floating Balance in the Imperial Bank			2,707	0	4					
on the 31st December, 1923										
Cash in Office, on the 31st December, 1923			218	14	0					
			<hr/>			<hr/>				
			Rs.	4,58,778	15	2	Rs.	4,58,778	15	2

Certified that the accounts for the year 1923  
have been audited and found correct.

I C. BOSE,

*Honorary Auditor.*

C. V. RAMAN,

*Honorary Secretary.*

To	Rs.	AS. P.	By	Rs.	AS. P.
Subscription Account	444	0 0	Govt. Securities 3½% General fund	2,000	0 0
Rent from shops	4,332	0 0	Commission account General fund	24	12 6
H. H. The Maharaja of Cooh-Behar.	300	0 0	Commission account Rupon Prof. fund	1	6 0
Professorship fund			Nikunja Garabini fund	0	3 0
Miscellaneous account	429	4 9	Contribution to Provident fund	185	6 9
Interest account, Garabini Fund	7,940	12 0	Building Repairs account	280	2 0
Rupon Prof. fund	190	0 0	Building Reconstruction acct.	359	1 0
Nikunja G. fund	17	8 0	Physics Research Scholarship acct.	447	8 0
Jatindra Ch. Prize fund	19	4 0	Scientific Instrument account General fund	3,619	14 0
Wood-bun fund	17	8 0			
Dr. Sircar Research medal fund	105	0 0	Municipal Tax account	1,757	6 0
Fees from students	12,616	15 0	Gas account	618	3 9
Bulletins sold account	42	14 6	Electric account	700	8 3
Provident fund account	722	7 0	Provident fund account	557	15 6
Old Material sold account	840	11 6	Workshop Petty Charges account	256	14 0
Dr. Sircar Memorial fund	962	8 0	Postage Stamp account	274	13 0
Deposit from students	15	0 0	Printing Charges	2,353	12 6
Vizianagram fund acct.	1,000	0 0	Laboratory Charges account	2,920	0 9

Suspense account	88	8	0	Library account	..	1,424	8	3
Discount account	..	844	1	Furniture account	...	760	5	9
Floating balance in the Imperial Bank on 31st December, 1922.	3,349	5	6	Electric Installation account	..	384	13	0
Cash in office on 31st December, 1922....	241	4	6	Deposit account		210	0	0
				Charges General account	.	792	1	9
				Botany class account	..	2,221	13	3
				Establishment account	..	8,273	14	9
				Miscellaneous account		49	10	6
				Suspense account		88	8	0
				Vizianagram fund account	..	600	0	0
				Water Pump Installation account		469	8	0
				Floating Balance in the Imperial Bank on the 31st December, 1923		2,707	0	4
				Cash in office on 31st December, 1923		218	14	0
						Rs. 34,559	0	7

Certified that the accounts for the year, 1923  
have been audited and found correct.

I. C. BOSE,  
*Honorary Auditor.*

C. V. RAMAN,  
*Honorary Secretary.*



## ANNUAL REPORT FOR THE YEAR 1924.

1. The Committee of Management beg to submit the following report showing the work done by the Association during the year under review.

2. The Physical Laboratory of the Association continued as usual to be a centre of active research in various branches of the science, and attracted workers from different parts of India and Burma. The following list of papers which were contributed from the Laboratory of the Association or published in its Proceedings during the year 1924 may serve as an indication of the volume of the research work in which the Association has co-operated.

Proceedings of the Association, Vol. VIII, Parts III and IV; Vol. IX, Part I.

(1) Electromagnetic Theory of the Scattering of Light in Fluids, Paper B—by K. R. Ramanathan, M.A., D.Sc., Assistant Lecturer in Physics, University College, Rangoon.

(2) The Electron Theory of Solids and the Rigidity of Metals—by Durgadas Banerji, M.Sc., Lecturer in General Physics, University College of Science, Calcutta.

(3) On the Fluorescence of Didymium in Glass—by N. C. Krishna Iyer, M.A., Professor of Physics, University College, Rangoon.

(4) The Colours of Colloids in Relation to the size of the Dispersed Particles—by Bidhubhusan Ray, D.Sc., Lecturer in Optics, Calcutta University.

(5) Colours of Chlorate of Potash—by L. A. Ramdas, M.A., Palit Research Scholar in the Calcutta University, Plate V.

(6) On the Colours of Mixed Plates, Part IV—by K. Seshagiri Rao.

(7) On the Maintenance of Vibrations by Variable Spring—by N. C. Krishna Iyer, M.A., Professor of Physics, University College, Rangoon.

(8) Scattering of Light by Smoky Quartz—by Nalini Kanta Sur, M.Sc.

(9) A. Study of the Critical Opalescence of Carbon dioxide—by D. K. Bhattacharyya, M.Sc., Professor of Physics, B. N. College, Patna.

(10) Infra-red Emission and Absorption of Potassium—by A. L. Narayan, M.A., D.Sc. and D. Gunnayya, M.A.

(11) Absorption of Electrically Luminescent Potassium Vapour—by A. L. Narayan, M.A., D.Sc., and G. Subramanyam, M.A.

(12) The Opalescence of Binary Liquid Mixtures—by J. C. Kameswar Ray, M.Sc., lately Palit Research Scholar, University of Calcutta.

(13) On the Modification of the laws of Emission of Ions from Metals by the Quantum Theory—by S. C. Roy, M.Sc., Research Scholar in Physics, Calcutta University.

(14) On the Colours shown by 'Nobili's Rings,'—by B. N. Chuckerbutti, D.Sc., P. R. Student, Assistant Professor of Physics, Calcutta University.

*Physical Review, 1924.*

Oblique scattering of Light in Gases and Liquids—by A. S. Ganesan.

*Philosophical Magazine, 1924.*

On the Mean Distance between Neighbouring Molecules in a Fluid—by Prof. C. V. Raman.

*Astrophysical Journal, 1924.*

On the Spectrum of Neutral Helium, II—by C. V. Raman and A. S. Ganesan.

*Nature.*

1. The Effect of Dispersion on the Interference Figures of Crystals—by Prof. C. V. Raman.

2. The Structure of Molecules in Relation to their Optical Anisotropy—by Prof. C. V. Raman.

Early in the year under review your Honorary Secretary proceeded to Bangalore where he attended the Science Congress as President of the section of Physics and as Hony. General Secretary of that organization. Besides delivering his presidential address, he also opened a discussion at a joint meeting of the physics, chemistry and agricultural sections, of the Theory of Surface Forces and also delivered a series of lectures to the general public at Bangalore and Madras.

Towards the end of February, was received the news of the election of your Honorary Secretary as a Fellow of the Royal Society of London. Shortly afterwards, he received an invitation from the British Association for the Advancement of Science to attend the meeting to be held at Toronto in Canada in August and to be the opener of a discussion on the scattering of light. The offer was backed by a substantial grant towards travelling expenses from the British Association; the Senate of the Calcutta University also appointed him as a Rashbehary Ghose Travelling Fellow to enable him to proceed to America.

After a brief visit to Simla as a delegate of the Calcutta University to the Universities Conference, your Honorary Secretary returned to Calcutta and then left for Bombay to sail by the Kaiser-i-Hind on the 7th June. Your Honorary Secretary was absent from India throughout the rest of the year under review and his duties were carried on in his absence by the two assistant secretaries.

Your Honorary Secretary besides taking part in the meetings of the British Association and the International



Congress of Mathematicians held in Toronto in August, represented the Association at the celebration of the Franklin Institute Centenary held in September in Philadelphia. The greetings of the Association were presented to the Institute amidst applause from a large gathering of the world's most renowned scientists.

The present report is hardly the place to give a detailed account of the activities of your Honorary Secretary during his absence from India, but it may be worth recording here that he was appointed as a research associate and visiting professor at the California Institute of Technology at Pasadena for the autumn session, 20th September to 16th December, 1924 and delivered an extensive series of lectures dealing principally with the researches on light-scattering carried on in the Laboratory of this Association.

Dr. K. R. Ramanathan of the Rangoon University came to our Association during the summer for continuing his investigations on the structure of molecules in relation to their optical anisotropy. A paper embodying his results was communicated to the Royal Society early in June, 1924.

Mr. A. S. Ganesan was awarded a research scholarship by the Madras University for continuing his researches on the Optical anisotropy of a series of organic vapours. A paper on the above subject will soon appear in the Philosophical Magazine. Soon after completing the above work he was awarded the Dominion Scholarship in Physics. He sailed for England early in September, 1924.

Mr. L. A. Ramdas continued his investigations on the scattering of light by liquid and solid surfaces and also studied the scattering of light by gases and gaseous mixtures at very high pressures. Towards the end of 1924 he investigated the excitation of the spectra of potassium during its spontaneous combination with chlorine gas.

Mr. K. S. Krishnan was engaged during the year in carrying out a systematic study of the molecular scattering of

light by seventy pure organic liquids. The important results obtained by him will shortly appear in the Philosophical Magazine.

Mr. Krishnapada Ghosh, Demonstrator in Physics in the Association Laboratory was working on the structure of soap bubbles.

Mr. Kedareshwar Banerji, was engaged in the study of the colour and structure of Amethyst quartz.

Mr. K. Veeramoney of Trivandrum worked in our Laboratory during the summer and carried out some preliminary work on X-rays and Crystal structure.

Mr. J. M. Das Gupta, Professor of Physics in the Mymensingh College, was working during the summer holidays on the refractometry of gases and liquids.

#### *Applied Electricity Class.*

The course of lectures on Applied Electricity by your Honorary Secretary commenced in 1923 was completed in the year under report. The lectures were attended to the finish by a group of interested students.

#### *Department of Chemistry.*

Mr. S. Venkateswaran, Chemical Assistant in the Government Test House, Alipore, was working during the year under report in our Chemical Laboratory in the evenings on the estimation and properties of ligno-cellulose. He also made preliminary studies on the scattering of light by solutions of gases in dust-free water.

#### *Botany Department.*

The required number of lectures in Botany for I.A. and I.Sc. students were delivered by Profs. Jyotish Chandra Pal and Raj Kumar Sen and the practical classes were held by these professors with the assistance of a demonstrator.

The test examination of the 2nd-year Botany Class was held in due time. The first three students will be awarded prizes. Their names are given in order of merit :—

1. Pradyatkumar Sinha.
2. Guru Prosad Ghose.
3. Satya Prakash Dey.

*Library.*

The following special additions to the Library were made during the year :—

1. Text Book on Wireless Telegraphy by Rupert Stanley, Vols. I and II.
2. Elements of Radiotelegraphy by Stone.
3. The Book of Wireless by Frederick Collins.
4. Robinson's Manual of Radiotelegraphy and Telephony.
5. Raussel's Wireless
6. Cassel's Wireless.
7. Crystal Receivers by Haris.
8. Theorie der Kristallstruktur by Dr. Arthur Schonflies.
9. Einfuhrung in die Theoretische Physik, Vol. I, Vol. II, Pt. I, by Dr. Clemens Schaefer.

The following publications were subscribed for as usual :—

1. Scientific American Monthly.
2. Nature.
3. Science Abstracts, A and B.
4. American Journal of Science.
5. Philosophical Magazine.
6. Botanical Gazette.
7. Annals of Botany.
8. Astrophysical Journal.
9. Chemical News.
10. Proceedings of the Royal Society, A and B
11. Transactions of the Royal Society, A and B.
12. Physical Review.

13. *Annalen der Physik*
14. *Physikalische Berichte.*
15. *Zeitschrift für Physik.*
16. *Physikalische Zeitschrift.*
17. *Encyklopadie der Mathematischen Wissenschaften.*
18. *Collegian.*

The Committee have to acknowledge with thanks the presentation of Journals and Periodicals in exchange from the following Societies and Institutions :—

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Faraday Society.
8. Franklin Institution.
9. American Geographical Society.
10. South African Association for the Advancement of Science.
11. *Sitzungsberichte of the Prussian Academy of Sciences, Berlin.*
12. *Sitzungsberichte of the Academy of Sciences, Vienna, Austria.*
13. University of Pennsylvania, Philadelphia.
14. Museum Journal of the University of Philadelphia.
15. *Journal de Physique et Radium of the Physical Society of France.*
16. Publications of the Royal Canadian Institute.
17. Technological and Scientific papers and Circulars of the Bureau of Standards.
18. University of Iowa.
19. University of Calcutta.
20. Calcutta Mathematical Society.

21. Government of India.
22. Government of Bengal.
23. Government of Mysore.
24. Government of Bombay
25. University of Bombay.
26. University of Allahabad
27. University of the Punjab.
28. Agricultural Research Institute, Pusa
29. Asiatic Society of Bengal.
30. Indian Institute of Science, Bangalore.
31. Editor, Indian Engineering.

The thanks of the Association are due to the Editors of the *Englishman*, *Forward*, *Bengalee*, *Servant* and *Basumati* for gratuitously supplying to the library of the Association their widely circulated daily newspapers and publishing in their columns the daily Meteorological reports of this Institution.

### *Workshop.*

The Workshop continued to function very satisfactorily. The mechanics turned out the following work during the year under report :—

1. Repairing dividing parts of the milling machine.
2. Coupling screw for fitting chuck in the big lathe.
3. Do. for Milling machine.
4. Two Milling cutters for pinion cutting with mandrel.
5. Mandrel for drill chuck for big lathe.
6. Angle plate for the same.
7. Two graduated circles for fitting nicols and double image prisms.
8. Fitting up wireless aerials.
9. Mounting air condenser.
10. Fitting up one tuning coil.
11. Steel tube for high pressure scattering work. .

12. One fine adjustable slit for concave grating.
13. Lathe bed for sliding concave grating.
14. Repairing 3<sup>11</sup> Telescope.
15. Repairing slide for big lathe and dividing the tool holder for the same.
16. Several steel boring tools.
17. Dividing the tool bed handle of the small lathe.
18. One Debye camera.
19. One Seigbahn metal X-ray tube

Besides the above, miscellaneous fittings and repairing jobs for the laboratory and workshop were carried out.

#### *Laboratory Equipment.*

The following were purchased during the year under report :—

1. One small transformer and alternating current generator for X-ray work.
2. One Gaede Box-Pump.

#### *Financial Position.*

On the 31st December 1924 the Association had in the custody of the Imperial Bank of India, Government securities of the value of Rs. 2,32,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal Fund, a floating balance in the bank of Rs. 3,657-5-6, and cash balance in the office of Rs. 3,698-6-0 amounting in all to Rs. 2,46,255-11-6.

On the 31st December 1923 the Association had in custody of Imperial Bank of India, Government securities of the value of Rs. 2,32,400-0-0 for the general fund, Rs. 6,000-0-0 for the Ripon Professorship fund, Rs. 500-0-0 for the Nikunja Garabini Medal Fund, a floating balance in the bank of

Rs. 2,707-0-4 and a cash balance in the office of Rs. 218-14-0, amounting in all Rs. 2,41,825-14-4.

3½% Government securities for Rs. 3,000 were also purchased for the Association early in December 1924. The transaction however appeared in the Bank's accounts for January 1925, and will therefore be included in the report for 1925.

The thanks of the Association are due to the following member who is kind enough to continue his annual subscriptions.

1. Babu Nirmal Chander Chander, M.A., B.L.

A special donation of Rs. 1,000 was received from H. H. The Maharaj of Trivandrum for which the Committee of Management offers its grateful acknowledgment.

*Acknowledgment.*

The thanks of the Association are due to their Honorary Engineers, Rai Krishna Chandra Banerjee, and Babu Bhabadev Chatterjee, to their Honorary Legal Advisers, Babus Jatindra Chandra Bose and Nirmal Chunder Chunder, to their Honorary Auditor, Babu Ishan Chandra Bose, their Honorary Secretary, Prof. C. V. Raman, and to their Honorary Assistant Secretaries, Babus Jyotish Chandra Pal and Ashutosh Dey for their gratuitous services.

During the year under report the Committee of Management thought it fit to appoint Babu Bhut Nath Chakravarty as Consulting Engineer to look after the construction, repairs and buildings of the Association. The thanks of the Association are extended to Babu Bhut Nath Chakravarty for his supervision and instructions to carry out certain important repairs of the buildings of the Association.

*Obituary.*

The Association sustained a most grievous loss during the year under report by the death of its President, Sir Asutosh Mookerjee. At a special general meeting held on

Thursday the 31st July, 1924, at 5-30 P.M., the following resolutions were accepted which conveyed the feelings of every one connected with the Association :—

That this meeting expresses deep regret at the untimely death of the President of this Association, Sir Asutosh Mookerjee, Kt, C.S.I, M.A., D.Sc., D.L., etc., and places on record its sense of the great loss the Association has sustained by the sad event. The death of Sir Asutosh Mookerjee has deprived the country of the invaluable services of one who was the greatest Educationist of the present day and who was a pre-eminently great man in various departments of life. He was connected with the Science Association first as a Lecturer, next as a member of the Committee of Management, then as a Vice-President and lastly as its President which office he held until the day of his death and this meeting places on record its grateful appreciation of the valuable services rendered by the illustrious deceased during his long connection with the institution.

2. That a portrait in oil of the late Sir Asutosh Mookerjee be kept in the Lecture Hall of the Association and that the Committee of Management be requested to arrange for the same.

3. That a copy of the above resolution be forwarded to Babu Rama Prasad Mookerjee, M.A., B.L., the eldest son of the deceased gentleman for information and for favour of communication to the other members of the bereaved family.

We have also to record with regret the death of Mr. S. K. Dutt, M.A., who was a life-member of the Association and who had taken much interest in our work and came forward to deliver lectures on Vector Analysis and Applied Electricity. His death deprives us of a genuine friend and scholar.

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*Balance Sheet as on the 31st December, 1924*

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*Dr.*

*Cr.*

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	Rs.	A. P.	Rs.	A. P.
Government Securities, General Fund ..	2,32,400	0 0	General Fund	3,93,478
Government Securities, Ripon Prof Fund.	6,000	0 0	Ripon Professorship fund	10,830
Government Securities, Nikunja G. Fund.	500	0 0	H. H the Maharaja of Cooch-Behar Fund	21,510
Range of shops, East Side	2,516	10 9	Hare Professorsup fund	1,025
Range of shops, West Side	2,308	5 0	Victoria Professorsup fund	1,000
Vizianagram Laboratory	40,900	14 0	Dr. Sircar Memorial fund	10813
Value of land and old building	31,650	11 9	Vizianagram fund	1,240
Lecture Hall and Gallery	23,465	5 3	Deposit Account	436
Observatory Room	3,310	9 9	Trivandrum donation account	1,000
Servants' Quarter	1,024	0 0	Provident fund account	3,648
Durwan's Room	303	13 9	Medal fund (Woodburn)	500
Bonus of Provident fund	1,922	0 0	„ (Dr. Sircar)	3,000
Contribution to P. F.	2,202	1 4	„ (Joy-Kisten)	9,339
			Prize fund (Nikunja-Garabini)	500

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Scientific Instrument account General F	46,648	7	8	..	(Jatindra Chandra)	550	0	0
" K. K. Tagore Fund	25,000	0	0	Interest account (Dr. Sircar Memorial Fund.		630	0	0
Botanical Instrument account	2,329	6	0	" (Ripon Prof fund)		6,095	4	3
Library account	25,996	2	4	Interest account (Nikunja-Garabini P. F.)		213	7	2
Tools and Implements account	161	12	3	Interest account (Wood-burn Medal fund)		124	0	0
Workshop instrument account	9,592	2	3	Interest account (Jatindra Chandra Prize fund)		115	15	0
Sir Richard Temple Prize account	245	0	0	Suspense account		7	6	0
Post Office Savings Bank account in connection with Employees Provident Fund account	183	6	0					
Floating balance in the Imperial Bank on the 31st December, 1924.	3,657	5	6					
Cash in office, on the 31st December, 1924.	3,698	6	0					
	4,66,056	7	7			4,66,056	7	7

(certified that the accounts for the year 1924, have been audited and found correct.

I C. ROSE,

*Honorary Auditor*

C V RAMAN,

*Honorary Secretary*

*Receipts and Expenditure during the year ending on 31st December, 1924*

RECEIPTS	Rs. A P.	EXPENDITURE	Rs. A P.
Subscription account	465 0 0	Commission account (general fund)	21 9 0
Rent from shops	1,332 0 0	Ripon Prof fund	1 6 0
Miscellaneous account	335 5 9	Nikunja Garabini fund	0 3 0
Interest account (General fund)	7,972 8 0	Contribution to Provident fund account	213 7 6
Interest account (Ripon Prof fund)	140 0 0	Buildings Repair account	509 0 9
" (Nikunja Garabini fund)	17 8 0	Buildings Reconstruction account	234 14 3
" (Jatendra Chandra Prize fund)	19 4 0	Scientific Instrument account	1,387 12 0
" (Woodburn Medical fund)	17 8 0	Municipal Tax account	2,466 2 0
" (Dr Mahendra Lal Sircar R M fund)	105 0 0	Physics Research Scholarship account	450 0 0
		Charges of Gas (Oriental Gas Co's) account	321 3 9
		Charges of Electric (Cal Elec. Supply Co) account	609 1 3
		Post Office Savings Bank account in connection with employees P. fund	183 6 0
		Workshop Petty charges account	415 1 0
		Postage stamp account	250 10 0
		Printing Charges account	1,495 15 0

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Fees from students account	10,806	4	0	Laboratory charges account	706	8	0
Bulletin, etc., sold account	26	9	2	Library account	1,063	1	9
Provident fund account	527	8	3	Furniture account	403	8	3
Old Material sold account	180	0	0	Electric Installation account	464	2	6
Dr Sircar Memorial fund account	229	12	0	Deposit account	15	0	0
H. H. the Maharaja of Travandrum donation account	1,000	0	0	Charges General account	716	11	3
Suspense account	88	8	0	Botany class account	2,175	13	6
Floating balance in the Imperial Bank on 31st December, 1923	2,707	0	4	Establishment account	7,305	6	3
Cash in office, on 31st December, 1923	218	14	0	Vizianagram fund account	100	0	0
				Miscellaneous account	191	12	3
				Suspense account	81	2	0
				Floating Balance in the Impl. Bank on the 31st December, 1924	3,657	5	6
				Cash in office on 31st December, 1924	3,698	6	0
TOTAL	29,138	9	6	TOTAL	29,138	9	6

Certified that the accounts for the year 1924 have been audited and found correct.

I C. BOSE.

*Honorary Auditor.*

C. V. RAMAN,

*Honorary Secretary.*



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